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Doctor's Dissertation

An Operations Research Approach to the Economic Optimization of a Kraft Pulping Process

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AN OPERATIONS RESEARCH APPROACH TO THE ECONOMIC OPTIMIZATION OF A KRAFT PULPING PROCESS

A thesis submitted by

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INTRODUCTION

Expectation of profit is the economic driving force motivating business activity in a free-enterprise economy. An increase in this profit for a given organization can be accomplished by discovering and following any of a number of courses of improved action. Operations Research* provides a scientific approach to the selection of those courses of action best fulfilling a particular objective set forth by management. Often this objective involves more efficient production, and, consequently, much effort has been spent on ways to decrease production costs by seeking "best" or "optimum" operating conditions.

The techniques now used for handling some of the more complicated Operations Research problems have been only recently applied in industry. The history of the development and use of some of these techniques can be found in references (2) and (3). Briefly, during World War II, large numbers of scientists and engineers from industry were hired by the Allied governments to help solve certain complex military problems. Upon conclusion of the war, these individuals returned to industry and carried with them their wartime experience. They found industrial problems to be well suited to the approach developed during the war. In this way, what had become known as "Operations Research" (O.R.) in military parlance was translated to peacetime industrial activities. Further developments in the business environment were especially rapid.

Today, most O.R. problems involve the mathematical description of complex industrial situations such that, by appropriate solution of

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* A general introduction to Operations Research is found in (1, 2, 3). Operations Research in the pulp and paper industry is discussed in (4, 5).

the mathematical model, management can be given quantitative information helpful in making better operating decisions. In this way, O.R. helps executives to fully concentrate their abilities on inherently intuitive problem areas demanding, primarily, so-called "business know-how."

The spirit of O.R. is not new. It is, for instance, very familiar to the industrial and chemical engineer through classical problems such as the Economic Lot Size. What is new in O.R. is the development of a systematic and confident approach to complex industrial problems, often using characteristic mathematical techniques and employing electronic computers for solution.

THE OPERATIONS RESEARCH APPROACH

The steps of the O.R. approach to an industrial problem may be considered as follows (1, 2):

1. Define the problem. Why is there dissatisfaction with the present operations and what alternative courses of action appear to hold most promise of being effective solutions to the problem, relative to a set of pertinent objectives.

2. Determine a suitable "measure of effectiveness" (often called the "objective") to be optimized. This nearly always involves the dollar sign. Usually, over-all company profits or net dollar return from some suboperation is to be maximized, or certain costs minimized. Thus, most O.R. optimizations are economic optimizations.

3. Elaborate a model to represent the system whose optimization is desired. A model may be defined as a device, physical or symbolic, "which behaves in a manner similar enough to some other system so that useful knowledge about the system may be gained from a study of the model" (6). Models are almost always necessary in industrial work since experimentation with full-sized industrial equipment disrupts production and is very costly in money and time. (However, see the discussion of "Evolutionary Operation" in Appendix VIII.) And sometimes industrial equipment is only contemplated in design or as replacements.

Usually, the most desirable model is the mathematical model, which employs mathematical statements to represent the system and enables responses to be calculated rather than be measured. The measure of effectiveness is expressed as a function of a set of variables at least one of which is subject to control. (The variables involved are often functionally interrelated so that they behave similarly to the active variables in the realistic system simulated.) As the variables are manipulated, their effectiveness in optimizing the objective is changed. Thus, the expression giving the effectiveness (E) of a set of levels for the independent, controllable variables $Y1$, $Y2$,.... may be written

$$E = E(Y1, Y2, \ldots).$$

Often there are restrictions imposed on the values of the independent variables, or functional restraints involving these variables, and such restraints are expressed by supplementary equations and/or inequations.

However, it may happen that operating, theoretical, or empirical information is not available for setting up the entire mathematical model. In this case, an experimental program using laboratory equipment to simulate the appropriate industrial processes and to allow for the determination of the desirable, supplementary operating information is often necessary.

4. Solve the problem: Determine the values of the independent (controllable) variables which optimize the objective (i.e., maximize the effectiveness of the system) subject to any restraints imposed on the system (equipment limitations, rigid management policy, operating limitations, minimum quality characteristics, market restrictions, legal limitations, etc.). Standard O.R. techniques are available for solving certain types of recurring problems, and it is desirable if the problem can be so typed [see references (1) and (3)]. Often, however, a combination of these techniques must be employed or other techniques devised.

The remaining steps in the O.R. approach can be done only on the industrial scene. They are:

5. Test the model and calculated solution obtained from it.

If adjustment is indicated, readjust the model, determine a new solution, and check again. A carefully chosen initial model may eliminate difficulties here.

6. Establish controls. The lack of effective control over certain variables might seriously invalidate the appropriateness of the original model. The need for a change in the original controllable variables to offset changes in uncontrollable variables must be recognized and a new optimum solution found. Automatic control systems actuated by electronic "optimizers" are destined to play an even more important part in future industrial operations. (See Appendix VIII.)

7. Implement the suggested solution through appropriate organizational channels, and establish a set of operating procedures so that those concerned with control of the operation can attain the optimum as easily as possible.

In carrying out the O.R. approach in industry, it has become customary to employ the "team approach," because the experiences and ideas of such a group having diversified professional backgrounds generally make it easier to set up and solve problems.

Finally, O.R. is importantly characterized by the "systems concept": that is, an attempt to study all the interdependent activities and variables related to the problem at hand, all the way through and even outside of the organization. In actual fact, though, virtually every "optimization" in O.R. is really a suboptimization--that is, an optimization of some part less than the whole [see reference (3)].

Usually, the suboptimum answer is different from that determined in the ideal, over-all optimum because all the factors have not been considered. Often, though, a system is naturally divided into parts which are independent or almost so, or the system is so complicated that even a suboptimization is an achievement.

OPTIMIZATION IN THE PULP AND PAPER INDUSTRY

There are relatively few optimization studies of any kind reported in the technical literature. Several companies in the pulp and paper industry have active O.R. groups which have solved a number of important problems. The details of these studies are not generally available. However, two examples of the application of linear programming to special situations in the pulp and paper industry have been published (7, 8).

One area in the pulp and paper industry in which Operations Research can be of considerable importance is pulping. The classical pulping studies are, in general, aimed at discovering the interrelationships among cooking variables, pulp yields, and quality characteristics, dissociated from the "systems concept" and quantitative economic considerations. Thus, the "optimum" conditions one finds discussed in the pulping literature are clearly not (nor do the authors imply them to be) the result of economic optimizations.

OPTIMIZATION OF THE KRAFT PULPING PROCESS

PRELIMINARY CONSIDERATIONS

The kraft pulping and recovery cycle operations comprise a reasonably isolated, yet complex, subsystem of an integrated papermaking

process. Figure 1 indicates this relationship.

In preliminary considerations concerning the development of an Operations Research approach for the optimization of a kraft pulping process, it was apparent that a fully developed mathematical model for the system could not be formulated without a careful and extensive study of kraft cooking reactions. In addition, it was realized that any model developed for a pulping system would be of a complicated (nonlinear) mathematical form. Optimizations of such models, while having considerable industrial importance, have not been studied to any great extent. It was therefore recognized that efficient optimization of a successfully developed pulping process model might be expedited by the development of a new approach to such optimizations.

These preliminary considerations led to the proposal of this thesis.

OBJECTIVES OF THE THESIS

The objectives of this thesis are:

(1) to demonstrate the applicability of, and

(2) to contribute to the implementation and understanding of the important analytical phases of model development and optimization in

an Operations Research approach to the economic optimization of a hypothetical, but realistic, kraft pulping process.*

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* The completed study itself (as opposed to the O.R. approach presented above) is, perhaps, more closely allied to so-called Systems Engineering than Operations Research. This is because the system involved deals predominantly with technical operations rather than the more intangible business considerations often characterizing Operations Research. See reference (9).

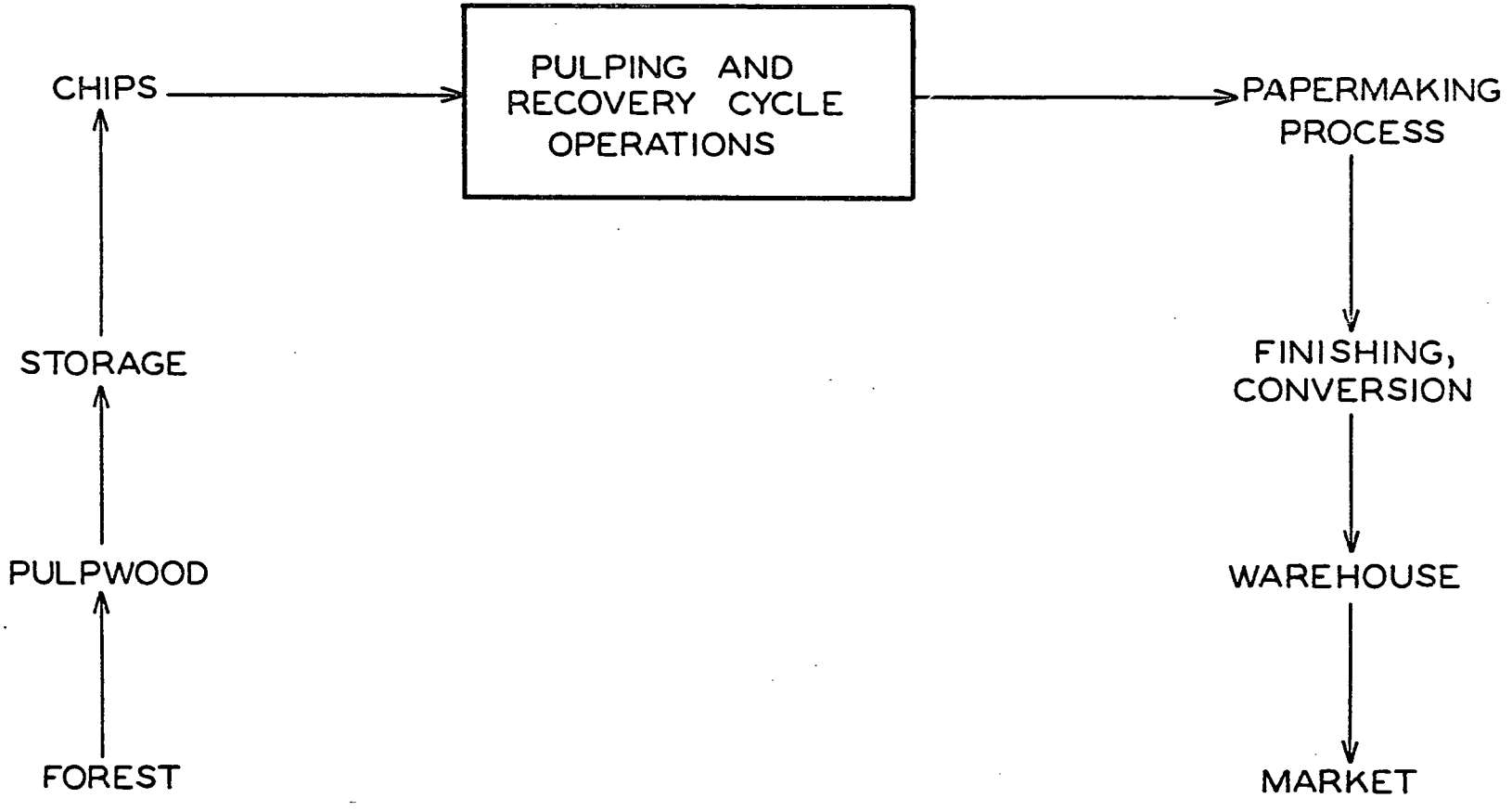

Figure 1. An Integrated Papermaking Process

THE HYPOTHETICAL KRAFT PULPING SYSTEM

The hypothetical system to be considered is shown in simplified form in Figure 2. It consists of the interrelated digester and recovery cycle operations for a kraft mill producing, under certain realistic conditions, a fixed daily amount of unbleached spruce pulp. Involved also are certain typical revenues and variable costs, and a number of realistic restraints. (The details of this system are developed later in this thesis.)

It should be noted in Figure 2 that a design cost (capital recovery plus interest for the evaporators) is included and is considered as a variable cost. Similarly, the restraint R7, setting a limit to the amount of capital available for purchasing evaporators, is a realistic restraint important in conjunction with decisions concerning the size (design) of a mill. These design considerations have been included to indicate that one approach to optimum design (and replacement, as well) can be exactly the same as that used to determine optimum operating conditions.

Because of this mixed cost situation, and because of the somewhat arbitrary way in which revenues, costs, and some restraints have been selected, any mathematical model developed for the hypothetical pulping system will be highly specific. This, of course, in no way detracts from a demonstration of the general utility of the Operations Research approach. Nor does it detract from any concepts developed in formulating and optimizing the model.

The "measure of effectiveness" for the hypothetical pulping system was chosen to be net dollar return. This is, simply: revenues minus variable costs for the process considered.

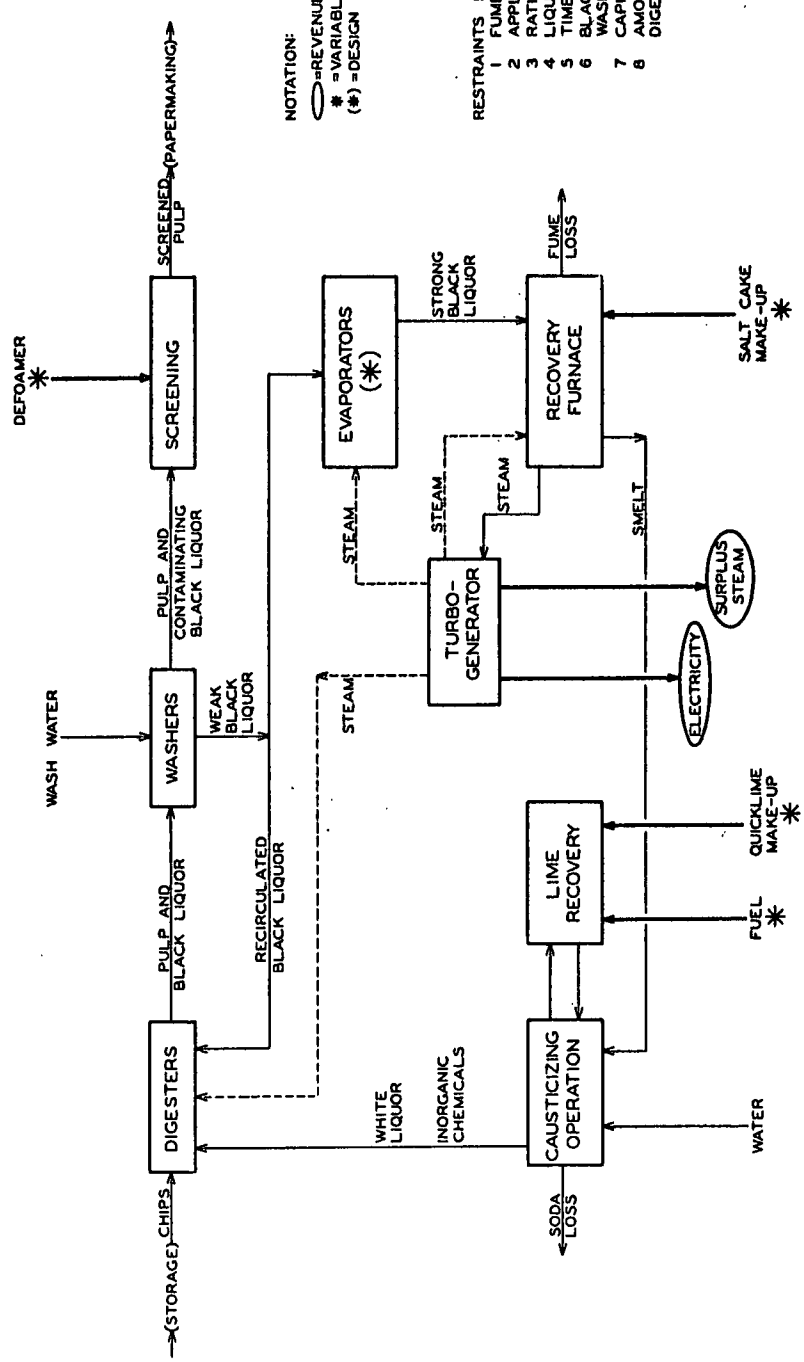

Figure 2. Simplified Flow Diagram of Hypothetical Kraft Pulping System

THE ECONOMIC OPTIMIZATION OF THE HYPOTHETICAL KRAFT PULPING PROCESS

DEVELOPMENT OF THE MODEL

It is generally desirable in optimization problems to represent the entire model in mathematical terms prior to optimization. This avoids experimentation involving sequential analysis of intermediate results during the optimization, and the consequent development of only the currently needed portions of the model. With complete prior quantification, the optimization can actually be accomplished more easily, and the model developed will have general utility in circumstances where certain portions of the system change due to temporary operating disruptions, cost and equipment changes, etc. Furthermore, such a model (in contrast to the very limited one developed in a sequential analysis) can often be almost directly incorporated as the framework of a more complete model of the same system, or as a complete portion of a more extensive model of an expanded system.

NEED FOR AND DEVELOPMENT OF A PULPING RATE EXPRESSION

Initially, in this study, preliminary material and energy balances indicated that all activities in the hypothetical pulping process, except the digester operation, were at least potentially capable of being quantified. As will be seen later, for complete prior quantification it is necessary to have an integrable rate expression interrelating all the important kraft cooking variables.

An investigation of the literature revealed the lack of any generally useful rate equation. However, there seemed to be evidence encouraging belief in the existence of such expressions and hinting at

how one might be derived.

Consequently, an investigation was undertaken wherein a rate expression appropriate for the economic optimization was theoretically developed and experimentally verified. A complete description of the development of this rate expression and of the experimental program designed for its verification appears in Appendices I and II. Also included is a discussion of the experimental results and the implications with respect to industrial and laboratory applications.

The theoretical development is based on a differential rate equation which has been found to be descriptive of certain constant-temperature, constant-concentration, kraft cooks (15). The equation is:

$$\frac{dL}{dt} = \alpha_2'' \, c(L - \alpha_1) \qquad (1)$$

where

L = % lignin in pulp at time, t,

c = constant concentration of cooking chemicals,

α_1 = % lignin "unavailable" for reaction, and

α_2'' = apparent rate constant at a given temperature.

In conventional, batch pulping operations, temperature and concentration are not constant, but vary during the cook. By employing the Arrhenius Equation to interrelate temperature and time for a given temperature-time schedule, and by developing and accounting quantitatively for the pattern of changing chemical concentration during a cook, an integrable cooking rate expression was developed. The integrated and experimentally verified form of this expression is:

$$\underline{t_t} = \frac{\ln \dfrac{[(\underline{K}\text{ no.})(0.292) - 2.53]\dfrac{\underline{Y}}{100} - 1.00}{25.00}}{\left(-5.22 \times 10^{-5}\right)\left(\underline{e}^{\,40.00 - (16{,}100/\underline{T_m})}\right)\left(\underline{c_i} - (0.0663)\dfrac{\underline{c_i}}{\underline{c_w}} - 5.05\right)} +$$

$$\underline{t_u}\left[1 - \frac{(\underline{T_m})^2}{16{,}100(\underline{T_m} - \underline{T_o})}\right]: \qquad (2)$$

This expression (to within $\pm 0.3\%$) relates, for the system considered, the total time of a cook ($\underline{t_t}$, min.) to initial digester temperature ($\underline{T_o}$, $^{\circ}$ abs.), time-up-to-temperature ($\underline{t_u}$, min.), maximum temperature ($\underline{T_m}$, $^{\circ}$ abs.), initial concentration ($\underline{c_i}$, g. active alkali/l.), chemical-to-wood ratio ($\underline{c_w}$, g. active alkali/g.), permanganate number ($\underline{K}$ no.), and pulp yield ($\underline{Y}$).

Certain limitations apply to this rate equation and, consequently to any pulping process model in which it is used to describe the cooking operation. For example, in the model to be developed, sulfidity must be maintained $\geq 28\%$. As indicated in Figure 2 and discussed in Appendix I, this restriction becomes a restraint ($\underline{R2}$) to which the optimization of the system is subject.

The use of the rate expression [Equation (2)] in the development of a mathematical model for the entire pulping process is discussed in the next section.

FORMULATION OF THE MATHEMATICAL MODEL FROM ENGINEERING BALANCES

As a result of having a rate expression interrelating the important kraft cooking variables and thereby quantitatively describing the digester operation, the entire hypothetical pulping process could be

quantified and its mathematical model developed. To do this, it was necessary to take material, energy, and economic balances over the whole system. These engineering balances were based on suitable assumptions and appropriate performance characteristics of the equipment, and for the operations involved. Thus, in addition to the pulping rate expression which describes the cooking operation, dilution curves for washing, steam economies in evaporation, the performance of the recovery furnace and steam turbines, causticizing efficiency in the causticizing operation, and quantitative expressions for the associated costs and revenues were all important factors in the formulation of a comprehensive mathematical model.

A detailed description of the hypothetical pulping system is given in Figure 3. The quantities indicated on this flow diagram resulted from material, energy, and economic balances based on an arbitrarily chosen, particular set of realistic operating conditions. Appendix III gives a detailed description of the assumptions and calculations made. From this specific base case, engineering balances, quantitatively describing and interrelating the operations of the pulping system, were established. These generalized balances, in turn, allowed the development of the mathematical model of the system.

Appendix IV describes the development of this model from the base case developed in Appendix III. Exhibit I shows the resulting mathematical model for the hypothetical kraft pulping process.

THE NATURE OF THE MATHEMATICAL MODEL

Number of Independent Variables

The model of Exhibit I consists of an effectiveness function

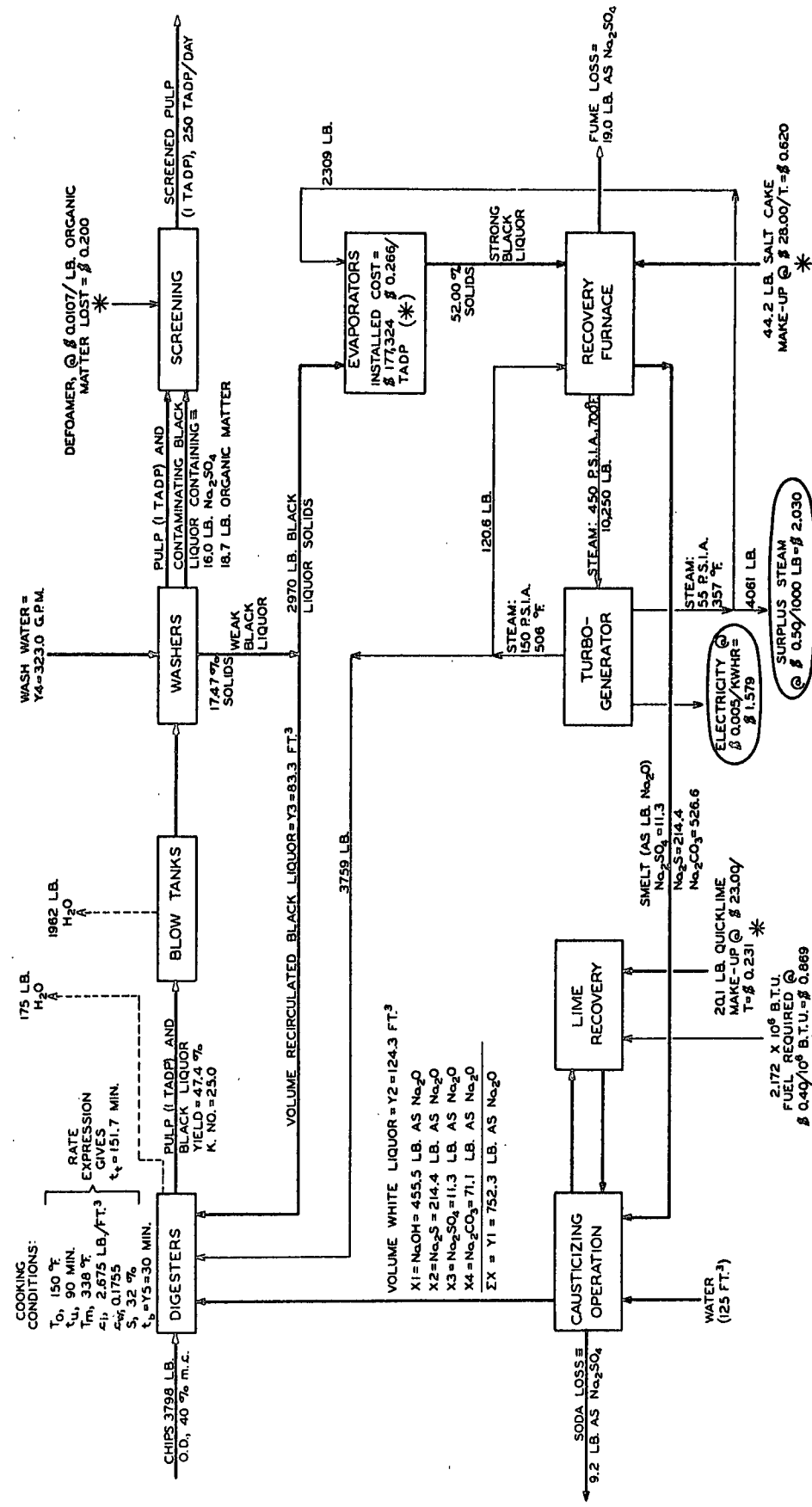

Figure 3. Detailed Flow Diagram of Hypothetical Kraft Pulping System

NOMENCLATURE FOR VARIABLES IN MODEL OF EXHIBIT I

C_e = installed cost of evaporators, dollars

c_i = initial active alkali concentration, lb./cu. ft.

c_w = initial active alkali-to-wood ratio, lb./lb.

E = measure of effectiveness (net return), dollars/TADP

H = heat in gross high-pressure steam generated, B.t.u./TADP

I = "water equivalent" of digester and contents, lb./TADP

ℓ = black liquor solids load to furnace, lb./TADP

L_N = unadjusted soda loss (as Na_2SO_4) from washers, lb./TADP

M = salt cake make-up (as Na_2O), lb./TADP

R_i = restraints

s = weight fraction solids in black liquor to evaporators and black liquor recirculated to digesters, lb./lb.

t_t = total time for a cook, min.

V_L = total volume of white and black liquors and moisture in chips, cu. ft./TADP

$X1$ = NaOH as Na_2O in white liquor before losses, lb./TADP

$X2$ = Na_2S as Na_2O in white liquor before losses, lb./TADP

$X3$ = Na_2SO_4 as Na_2O in white liquor before losses, lb./TADP

$X4$ = Na_2CO_3 as Na_2O in white liquor before losses, lb./TADP

$Y1$ = total load of inorganic chemical as Na_2O in white liquor before losses, lb./TADP

$Y2$ = volume of white liquor to digesters, cu. ft./TADP

$Y3$ = volume of black liquor to digesters, cu. ft./TADP

$Y4$ = rate of fresh wash water to washers, g.p.m.

$Y5$ = time between cooks, min.

ΣX_a = actual total load of inorganic chemical in white liquor before losses, lb./TADP

ΣX_s = actual total load of smelt from recovery furnace unit, lb./TADP

EXHIBIT I.
THE MODEL

Basis: 1 Ton of Air-Dried Pulp (TADP)

Effectiveness Function = net return ($) = revenues ($) - variable costs ($) =

$$\underline{E} = (5.843)(10^{-7})\underline{H} - (1.170)(10^{-4})\underline{I} - (2.358)(10^{-5})\underline{\ell} - \frac{(\underline{\ell}/\underline{s} - \underline{\ell}/0.52)10^{-4}}{1.104 - (0.72)\underline{s}} -$$

$$(1.365)(10^{-1}) - (1.502)(10^{-6})\underline{C_e} - (3.21)(10^{-2})\underline{M} - (5.08)(10^{-4})\underline{X1} -$$

$$(4.77)(10^{-3})(\underline{k_9})\underline{X1} - \frac{(37.48)\underline{L_N}}{(0.995)\sum \underline{X_a} + 1998} \qquad (3)$$

Restraints:

$$\underline{R1} = \underline{K_1} - \frac{(8.3)\underline{Y1}}{752.3} \geq 0 \qquad \text{(fume loss limitation)} \qquad (4)$$

$$\underline{R2} = \underline{X2} - \frac{(K_2)\underline{X1}}{(1 - \underline{K_2})} \geq 0 \qquad \text{(applicability of Model restriction)} \qquad (5)$$

$$\underline{R3} = (\underline{K_3})\underline{Y2} - \underline{Y3} \geq 0 \qquad \text{(limitation on ratio of black to white liquor)} \qquad (6)$$

$$\underline{R4} = \underline{V_L} - \underline{K_4} \geq 0 \qquad \text{(restriction on liquor-to-wood ratio)} \qquad (7)$$

$$\underline{R5} = \underline{Y5} - \underline{K_5} \geq 0 \qquad \text{(limitation on time between cooks)} \qquad (8)$$

$$\underline{R6} = \underline{K_6} - \frac{(.3496)\underline{L_N}}{(0.995)\Sigma \underline{X_a} + 1998} \geq 0 \qquad \text{(restriction on black liquor contamination in washed pulp)} \qquad (9)$$

$$\underline{R7} = \underline{K_7} - \underline{C_e} \geq 0 \qquad \text{(capital procurement limitation)} \qquad (10)$$

$$\underline{R8} = \frac{n(15,553)}{\underline{t_t} + \underline{Y5}} - 110.6 - \underline{V_L} \geq 0 \qquad \text{(limitation to the amount of liquor plus chips per digester charge)} \qquad (11)$$

In addition: All independent variables ($\underline{Y1}$, $\underline{Y2}$, $\underline{Y3}$, $\underline{Y4}$, $\underline{Y5}$) ≥ 0. The economics of the process makes mathematical statements of these "non-negativity" restraints unnecessary.

Subsidiary Equations:

$$\underline{H} = (1.413)(10^7) - (1328)\Sigma\underline{X}_a - (531)\Sigma\underline{X}_s + \frac{[(2324)\Sigma\underline{X}_a - (2.874)(10^7)]\underline{L}_N}{(0.995)\Sigma\underline{X}_a + 1998} \quad (12)$$

$$\underline{I} = 3623 + (64.4)\underline{Y2} + (58.4)\underline{Y3} + \frac{n(36,578)}{\underline{t}_t + \underline{Y5}} \quad (13)$$

$$\underline{\ell} = (0.995)\Sigma\underline{X}_a + 1998 - (1.75)\underline{L}_N \quad (14)$$

$$\underline{s} = \underline{\ell}/[(0.995)\Sigma\underline{X}_a + (60.8)\underline{Y2} + (48)\underline{Y4} - (0.1121)\underline{I} - 5095] \quad (15)$$

$$\underline{C}_e = 148,000 - (331,000)\underline{s} + (40)\underline{\ell} - (61)\underline{s}\underline{\ell} \quad (16)$$

$$\underline{M} = \frac{(12.3)\underline{Y1}}{752.3} + \frac{(1.75)\underline{L}_N(0.995)\underline{Y1}}{(0.995)\Sigma\underline{X}_a + 1998} \quad (17)$$

$$\underline{L}_N = \frac{k_6}{(0.024)\underline{Y4} - k_7} + k_8 \quad (18)$$

$$\underline{Y1} = \left\{k_1 - [(4.782)(10^{-2})(\underline{Y1} - \underline{X3}) + (1.956)(10^{-1})(\underline{Y1} - \underline{X3})^2/\underline{Y2} + (6.376)(10^{-1})\underline{X2} + (1.594)\underline{X3}]\frac{1}{(100)\underline{Y2}}\right\}(\underline{Y1} - \underline{X2} - \underline{X3}) \quad (19)$$

$$\underline{Y2} = (19)\underline{Y3} \quad (20)$$

$$\underline{Y3} = \frac{(3.535)(10^{-4})(\underline{Y1})^2 + (5.311)(10^{-1})\underline{Y1} + (8.705)(10^{-2})\underline{L}_N(\underline{Y1})}{(5.2)(10^{-2})\underline{Y1} + 78 + (2.377)(10^{-3})\underline{L}_N(\underline{Y1})} \quad (21)$$

$$\underline{Y4} = \underline{Y1} - (\underline{X1} + \underline{X2} + \underline{X3}) \quad (22)$$

$$\sum \underline{X}_a = (1.290)\underline{X}1 + (1.258)\underline{X}2 + (2.290)\underline{X}3 + (1.710)\underline{X}4 \quad (23)$$

$$\sum \underline{X}_s = (1.710)\underline{Y}1 - (4.52)(10^{-1})\underline{X}2 + (5.80)(10^{-1})\underline{X}3 \quad (24)$$

$$\underline{t}_t = \frac{\underline{k}_2}{\underline{c}_i - \underline{k}_3 \frac{\underline{c}_i}{\underline{c}_w} - \underline{k}_4} + \underline{k}_5 \underline{V}_L \quad (25)$$

$$\underline{c}_i = \frac{(\underline{X}1 + \underline{X}2)(0.995)}{\underline{V}_L} \quad (26)$$

$$\underline{c}_w = \frac{(\underline{X}1 + \underline{X}2)(0.995)}{3798} \quad (27)$$

$$\underline{V}_L = \underline{Y}2 + \underline{Y}3 + 41.6 \quad (28)$$

Parameters:

fixed parameters:

- $\underline{k}_1 = 0.950$
- $\underline{k}_2 = 96.82$
- $\underline{k}_3 = 0.0663$
- $\underline{k}_4 = 0.3153$
- $\underline{k}_5 = 0.321$
- $\underline{k}_6 = 12.5$
- $\underline{k}_7 = 4.62$
- $\underline{k}_8 = 12.0$

fixed parameters:

- $\underline{K}_1$ = 10.0, maximum allowable fume loss = 10 lb./TADP
- $\underline{K}_2$ = .28, minimum sulfidity allowable for Model to be applicable = 28%
- $\underline{K}_3$ = 1.5, maximum ratio of black to white liquor = 1.5
- $\underline{K}_4$ =213.1, minimum allowable liquor-to-wood ratio = 3.5 ml./g.
- $\underline{K}_5$ = 25.0, minimum time required between cooks = 25 min.

parameters adjustable for the purpose of model alteration:

- $\underline{k}_9$ = cost of lime kiln fuel, $/10^6 B.t.u.
- $\underline{n}$ = number of digesters
- $\underline{K}_6$ = maximum allowable black liquor contamination in washed pulp, lb. B.L. organic matter/TADP
- $\underline{K}_7$ = maximum capital available for purchasing evaporators, $

(revenues minus variable costs); eight realistic, functional restraints; and a number of "subsidiary equations" and parameters. For the hypothetical pulping system considered, there are five more variables in the subsidiary equations (and thus in the effectiveness and restraint functions) than there are subsidiary equations for their determination. Thus, there are five independently adjustable variables, and, while they may be arbitrarily chosen in a number of ways, they are defined here as follows:

$\underline{Y}1$ = total load of inorganic chemical as Na_2O in white liquor before losses

$\underline{Y}2$ = volume of white liquor to digesters

$\underline{Y}3$ = volume of black liquor to digesters

$\underline{Y}4$ = rate of fresh wash water to washers

$\underline{Y}5$ = time between cooks at each digester

(Values of these five independent variables for the base case of Appendix III are indicated in Figure 3.)

Effectiveness Function and Restraints as Implicit Functions of the Independent Variables Alone

If values are assigned to the adjustable parameters in the model (Exhibit I), all the components of the effectiveness function and all of the restraints are, by means of the subsidiary equations, defined implicitly in terms of the independent variables ($\underline{Y}$'s) alone. This can be demonstrated for a typical component of the effectiveness function and a representative restraint by interrelating the selected subsidiary equations displayed in Exhibit II.

EXHIBIT II

EQUATIONS INDICATING HOW MODEL CAN BE EXPRESSED IN TERMS OF THE INDEPENDENT VARIABLES ALONE

$$\underline{M} = \frac{(12.3)\underline{Y1}}{752.3} + \frac{(1.75)\underline{L_N}(0.995)\underline{Y1}}{(0.995)\Sigma\underline{X_a} + 1998} \tag{17}$$

$$\underline{L_N} = \frac{12.5}{(0.024)\underline{Y4} - 4.62} + 12.0 \tag{29}$$

$$\Sigma\underline{X_a} = (1.290)\underline{X1} + (1.258)\underline{X2} - (2.290)\underline{X3} + (1.710)\underline{X4} \tag{23}$$

$$\underline{X1} = \left\{0.950 - [(4.782)(10^{-2})(\underline{Y1} - \underline{X3}) + (1.956)(10^{-1})(\underline{Y1} - \underline{X3})^2/\underline{Y2} + (6.376)(10^{-1})\underline{X2} + (1.594)\underline{X3}]\frac{1}{(100)\underline{Y2}}\right\}(\underline{Y1} - \underline{X2} - \underline{X3}) \tag{19}$$

$$\underline{X2} = (19)\underline{X3} \tag{20}$$

$$\underline{X3} = \frac{(3.535)(10^{-4})(\underline{Y1})^2 + (5.311)(10^{-1})\underline{Y1} + (8.705)(10^{-2})\underline{L_N}(\underline{Y1})}{(5.2)(10^{-2})\underline{Y1} + 78 + (2.377)(10^{-3})\underline{L_N}(\underline{Y1})} \tag{21}$$

$$\underline{X4} = \underline{Y1} - (\underline{X1} + \underline{X2} + \underline{X3}) \tag{22}$$

$$\underline{R8} = \frac{n(15,553)}{\underline{t_t} + \underline{Y5}} - 110.6 - \underline{V_L} \geq 0 \tag{11}$$

$$\underline{t_t} = f(\underline{Y1}, \underline{Y2}, \underline{Y3}, \underline{Y4}, \underline{Y5}) \tag{30}$$

$$\underline{V_L} = \underline{Y2} + \underline{Y3} + 41.6 \tag{28}$$

$$\underline{E} = \text{Effectiveness} = \text{Revenues} - \text{Costs} = E(\underline{Y1}, \underline{Y2}, \underline{Y3}, \underline{Y4}, \underline{Y5}) \tag{31}$$

$$\underline{R_i} = \underline{i}^{th}\ \text{Restraint} = R_i(\underline{Y1}, \underline{Y2}, \underline{Y3}, \underline{Y4}, \underline{Y5}) \geq 0,\ \underline{i} = 1,2.....,8 \tag{32}$$

The cost of salt cake make-up is considered as a representative and familiar component of the model's effectiveness function. Knowing the cost per ton of salt cake, it is necessary to express the amount of salt cake required, for any given set of operating conditions, as a function of the corresponding independent variables. The amount of salt cake required, $\underline{M}$, is expressed in the generalized material balance by Equation (17). See Exhibit II. This equation involves, besides the independent variable $\underline{Y}1$, the two variables $\underline{L}_N$ and $\Sigma\underline{X}_a$. ($\underline{Y}1$ is the total load of inorganic chemical as $\underline{Na_2O}$ in the white liquor, before losses; $\underline{L}_N$ is related to the inorganic chemical lost from the washers; $\Sigma\underline{X}_a$ is the actual total load of inorganic chemical in the white liquor, before losses.) Each of the two variables, $\underline{L}_N$ and $\Sigma\underline{X}_a$, must be expressed ultimately as a function of the $\underline{Y}$'s only. This is done for $\underline{L}_N$ by Equation (29) which is essentially a dilution curve equation relating $\underline{L}_N$ to $\underline{Y}4$ (rate of fresh wash water to washer system).

The quantity, $\Sigma\underline{X}_a$, is defined by Equation (23), where

$\underline{X}1$ = NaOH as Na_2O in the white liquor before losses,
$\underline{X}2$ = Na_2S as Na_2O in the white liquor before losses,
$\underline{X}3$ = Na_2SO_4 as Na_2O in the white liquor before losses, and
$\underline{X}4$ = Na_2CO_3 as Na_2O in the white liquor before losses,

and the numerical coefficients represent the ratio of actual weight to weight as Na_2O for each component.

Equation (23), in conjunction with the following four equations (19-22), defines $\Sigma\underline{X}_a$ as a function of the $\underline{Y}$'s and $\underline{L}_N$. [Equation (19) is essentially a causticizing efficiency condition of 95% reduction in the furnace. Equation (21) results from the combination of several material balances, while Equation (22) is, in effect, the definition of $\underline{Y}1$.] As indicated above, $\underline{L}_N$ is a function of $\underline{Y}4$ only [see Equation (29)], so that by means of the subsidiary equations, $\underline{M}$ can be expressed as a function of the independent variables alone.

A typical restraint, $\underline{R}8$, (recognizing a limitation to the amount of chips and liquor that can be put in digesters of a given size) is expressed in the model and in Exhibit II by Equation (11). The experimentally verified rate expression gives $\underline{t}_t$ (total time for a cook) as a function of the kraft cooking variables. In the hypothetical pulping system, some of these variables are constant; the remaining cooking variables, and thus $\underline{t}_t$, can be expressed ultimately in terms of the $\underline{Y}$'s [Equation (30)] in a manner similar to that shown for $\Sigma\underline{X}_a$ above. Then, since $\underline{V}_L$, the total volume of liquor, is,

by Equation (28), a function of independent variables alone, R8 is seen to be expressed essentially in terms of the Y's. [Restraint R8 is essential in the system and is one reason the pulping rate expression had to be developed. The "n" in Equation (11) is a parameter characterizing the system and so is fixed for a given optimization.]

In this manner, the whole model--that is, all costs and revenues comprising the effectiveness function, and all the restraints considered--can be ultimately expressed in terms of the independent variables alone [Equations (31), (32)].

Nonlinear Nature of the Model

The nature of a mathematical model in reference to its optimization (discussed in a following section) is determined by its characteristics when explicitly expressed in terms of the independent variables alone. Such explicit expression can be accomplished for the pulping system model of Exhibit I by actually carrying out the process discussed in the preceding section. Doing this, the effectiveness function and four of the restraints (R2, R6, R7, and R8) are seen to be complicated nonlinear functions of the independent variables (Y's). Thus, the over-all model is classified as nonlinear. More descriptively, the model represents a nonlinear, restrained system.

Adjustable Parameters

The adjustable parameters were incorporated in the model to provide for flexibility in the optimization studies. Their use in this connection is discussed in the next section.

OPTIMIZATION

The optimization of the mathematical model representing the hypothetical pulping system constituted the final phase of this thesis. Optimization consists of the determination of the values of the model's independent variables (Y's) which maximize the effectiveness function subject to nonviolation of the restraints.

Optimizations can be accomplished in a number of ways depending on the particular nature of the effectiveness function, the presence or absence of restraints, the nature of the restraints when present, the dimensions and complexity of the problem, the accuracy desired in the final solution, etc. (In addition, when computers are used, computer speed and storage capacity are considerations.)

Thus, when the effectiveness function and any restraints involved are linear, standard methods of linear programming can be used to seek an optimum. On the other hand, a general case for optimization occurs when the effectiveness function and at least some of the restraints are relatively complicated, nonlinear expressions. The pulping system model of this thesis is an example of this general case. Such nonlinear situations have considerable industrial importance.

SOME APPROACHES TO THE OPTIMIZATION OF NONLINEAR SYSTEMS

When the effectiveness function is nonlinear and subject to no restraints (this probably seldom happens in realistic situations), the approximate gradient technique of the Method of Steepest Ascents can be used to seek an optimum (10). (If dimensionality is not too great, ordinary calculus can be used.) The Method of Steepest Ascents

allows for the approximate calculation of the steepest path up to the top of the effectiveness surface so that the maximum is arrived at very efficiently. The thin, solid line in Figure 4 indicates, for a three-dimensional case [$\underline{E} = E(\underline{X}_1, \underline{X}_2)$], this path (I, 4, 5, 2, 1) which, ideally, is always perpendicular to the contour lines (lines of constant $\underline{E}$). Point I is an arbitrarily chosen starting point.

When restraints apply, Lagrange multipliers may be used in smaller problems (1, 11, 12). For larger ones, one approach is to apply the Method of Steepest Ascents until a limiting value of a restraint is reached. From this point on, an efficient procedure depends upon the nature of the model--in particular, the nature of restraints. Thus, when a single restraint is involved, like $\underline{R}'$ (which represents a maximum value for the independent variable $\underline{X}_1$) in Figure 4, the optimization may be completed by moving in the direction of steepest ascent with this variable held constant at its limiting value. The over-all path of the optimization then becomes I, 4, 5, 2, 3. (The arrows from the dashed restraint curves in Figure 4 point into the region of allowable solution.)

However, suppose a single restraint, $\underline{R}''$ (a more complicated functional restraint), is involved (again, see Figure 4). Following the path of steepest ascent soon results (at point 4) in a violation of this boundary. Using the approximate gradient method alone, one might proceed farther up the path of steepest ascent in hopes that the restraint would become noncritical at the optimum (as actually happens in the illustration). But in a more complex problem, since neither the nature of the effectiveness surface nor that of the restraints may be known, this is risky.

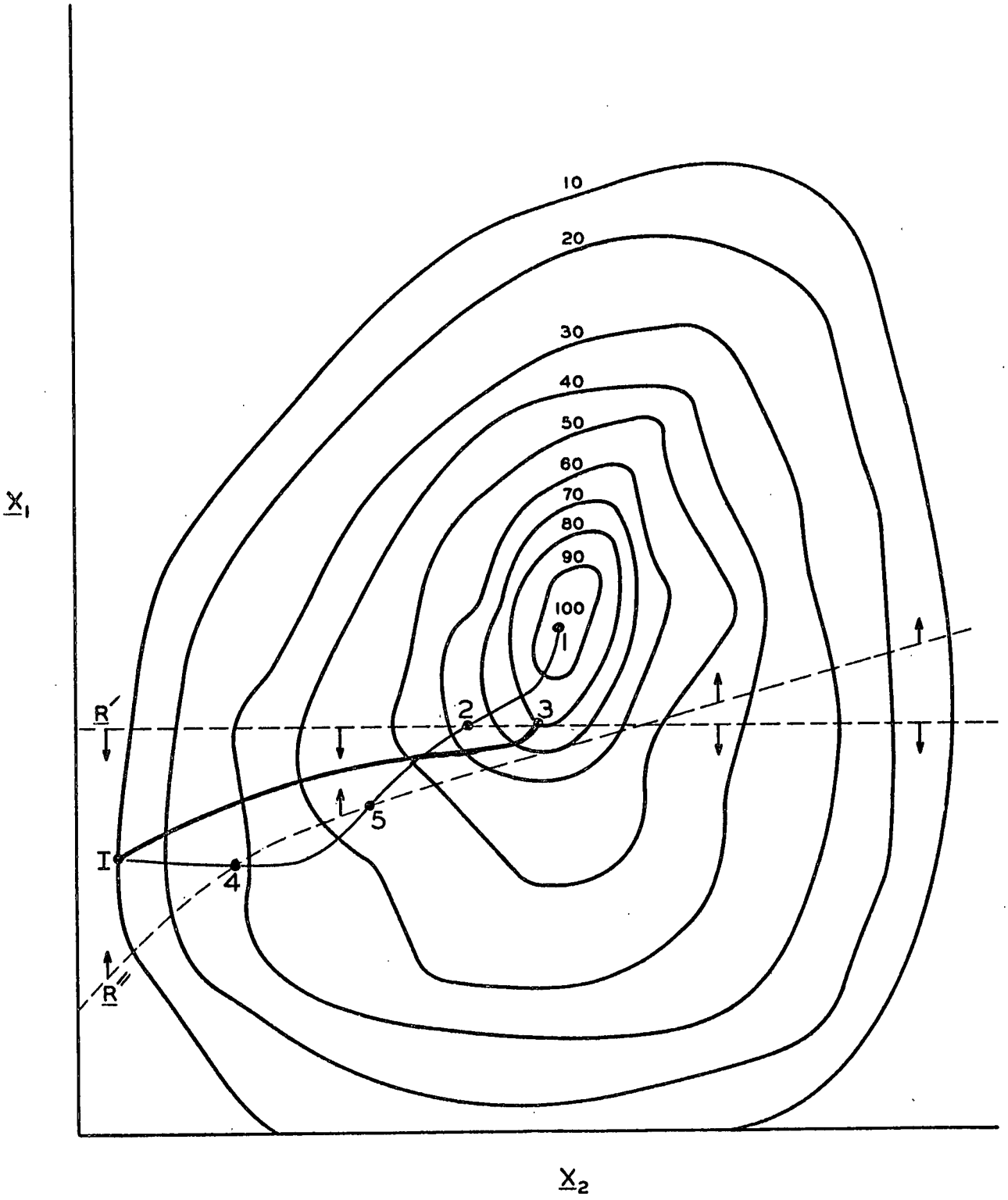

Figure 4. Contour Diagram of $\underline{E} = E(\underline{x}_1, \underline{x}_2)$ Showing Paths of Ascent and Restraints

As another approach to the above situation, it is possible, by means of a series of linear approximations to the nonlinear effectiveness and restraint surfaces, to apply linear programming sequentially (13). But this approach can be somewhat inefficient.

Still other techniques, such as a combination of linear programming and "search" theory (14) and the Monte Carlo method have been suggested or used in certain complex nonlinear situations.

THE CREATED RESPONSE SURFACE TECHNIQUE: A NEW APPROACH TO THE OPTIMIZATION OF NONLINEAR, RESTRAINED SYSTEMS

A different approach to the general problem of optimization of nonlinear, restrained systems was developed as a portion of this thesis. This new approach, called the Created Response Surface Technique (CRST), converts a restrained optimization problem into a series of nonlinear, unrestrained optimization problems. With both restraints, $\underline{R}'$ and $\underline{R}''$, applying in Figure 4, the CRST takes a modified path of ascent (heavy, solid line) which, while maximizing $\underline{E}$ as quickly as possible, at the same time automatically steers clear of the restraints and thus prevents their violation. This is accomplished by creating an artificial response function, $\underline{A}$, which combines the effectiveness function, $\underline{E}$, and a penalty, $\underline{P}$, for being too close to the limiting (zero) value of any of the restraints, $\underline{R}_i$. (Note, all of the restraints in the model of Exhibit I are expressed in the form: $\underline{R}_i \geq 0$.) This new function is defined as follows:

$$\underline{A} = \underline{E} - \underline{r}\,\underline{P} = \underline{E} - \underline{r} \sum_{\underline{i}} \frac{\underline{W}_i}{\underline{R}_i}. \qquad (33)$$

In this equation, the $W_i > 0$ and r is an adjustable constant ≥ 0 which weights the penalty in relation to E. For each value of r, there is an associated A-function or A-surface. These A-functions are unrestrained, since they include the restraints. They are a composite of the effectiveness function and any restraints applying.

During optimization by the CRST, the optimum solution is approached by following the maxima of a succession of A-surfaces created by the stepwise reduction of r. Each A-surface maximum is approximated by the Method of Steepest Ascents. In attempting to maximize any particular A-function by appropriate manipulation of the independent variables, an ever-increasing penalty (tending to decrease A) is incurred as any restraint boundary is approached (i.e., as any $R_i \rightarrow 0$; W_i/R_i, $P \rightarrow \infty$). In this way, undesirable changes in the independent variables are assuredly avoided during optimization. Near the actual optimum, by setting $r = 0$, A becomes identical with E. Then the approximate optimal solutions are developed on the true effectiveness surface and allowed, penalty-free, on, or very close to, any critical restraint boundaries.

A complete development of the CRST appears in Appendix V, which includes two examples illustrating the concepts involved, the computational logic, and the calculations required.

APPLICATION OF THE CRST TO THE OPTIMIZATION OF THE HYPOTHETICAL KRAFT PULPING SYSTEM

In order to extend the study of the nature and utility of the CRST as an efficient method for optimizing nonlinear, restrained systems, this new approach was applied to the optimization of the hypothetical kraft pulping system.

The adjustable parameters built into the pulping system model (see Exhibit I) are related to costs and the location of several restraint boundaries. Their adjustment provides for an easily changed model corresponding to a somewhat altered system. By changing these parameters and other initial conditions, and by varying certain arbitrary features of the CRST (e.g., the values of the W_i's, the r-reduction schedule, etc.), a series of revealing optimizations could be studied.

Use of a Computer

Because of the magnitude and the repetitive nature of the calculations required, and because of the extent of the optimization studies planned, use of a digital computer was indicated. The development of an IBM 650 computer program for optimizing the hypothetical kraft pulping system by means of the CRST is discussed in Appendix VI.

Results

As a result of the optimization studies, the expected ability of the CRST to efficiently improve the effectiveness of the pulping system model was demonstrated. Specific results of optimizations must be considered as highly characteristic of the particular system optimized and the effectiveness of the starting point of the optimization. With this in mind, the effectiveness of the hypothetical kraft pulping process operating, for example, as in the base case of Appendix III (see also Fig. 3), could be improved by over $98,000 per year. (Regardless of the amount of improvement in effectiveness, there are always many indirect benefits resulting from industrial optimizations.

These are discussed in the Conclusions.)

A planned and important outcome of the optimization studies was the accumulation of observations and information making possible the formulation of guide rules expected to be of general utility in the application of the CRST to other optimization problems.

A detailed discussion of the conditions and results of the various optimization studies appears in Appendix VII. A discussion of the use of the CRST (based largely on the results of Appendix VII) for general, nonlinear, restrained optimizations appears in Appendix VIII. Included also in this appendix is a discussion of the solution of linear programming problems by the CRST, a description of an alternate way in which the CRST can be used to optimize restrained systems, and some applications to the optimization and control of nonlinear, restrained systems in the laboratory and plant by using the CRST in experimental designs.

GENERAL SUMMARY

One name given to a systematic approach to broad industrial problems is "Operations Research." Operations Research usually involves setting up a mathematical model which simulates the operating interrelationships of a given process or system. By appropriate manipulation of the variables in the model (counterparts of the system's controllable operating variables), the conditions for maximizing the profitability of the system can be determined.

This thesis describes an Operations Research approach to the maximization of net dollar return from the operation of a hypothetical but realistic kraft pulping process. The system includes the interrelated digester and recovery cycle operations and the associated revenues and costs involved in the manufacture of an unbleached grade of spruce kraft pulp.

In order to represent the entire pulping process by a mathematical model, it was necessary to develop from fundamental considerations a suitable rate expression interrelating all the important kraft cooking variables. A main feature of the development is a quantitative accounting for the decreasing alkali concentration during a cook.

Virtually the same rate equation as the one hypothesized was precisely verified, experimentally, by making a series of carefully controlled and analyzed cooks. The verified rate expression predicts, for the system studied, total time for a cook to within $\pm 0.3\%$ (95% confidence limits are ± 1 minute) as a function of initial temperature, time-up-to-temperature, maximum temperature, initial concentration, chemical-to-wood ratio, permanganate number, and yield. The equation can be used for the

system studied (or as part of a pulping process model) only within certain rather broad limitations. The most important of these seems to be that sulfide concentration during the cook must always be high enough to assure that the rate-controlling reaction involves sodium hydroxide rather than sodium sulfide or a derivative thereof.

This pulping rate expression, and extensive material, energy, and economic balances taken throughout the system, allowed the net dollar return (revenues minus costs) to be expressed as a function of the system's controllable operating variables. This expression for net return, and similar mathematical expressions representing certain realistic restrictions which cannot be violated, comprise the mathematical model of the pulping system.

The immediate objective of the economic optimization was to determine the values of the controllable operating variables which maximize the net return, subject to nonviolation of the restraints considered.

The mathematical model, besides having restraints, is nonlinear. This is representative of a very general and industrially important situation. A new approach to the solution (optimization) of this type of model was developed as part of the thesis. This approach, called the Created Response Surface Technique, is based, essentially, on steepest ascents up a succession of created response surfaces within the solution space. The most important characteristic of the new approach is that it assuredly avoids violation of restraints during an optimization.

Using a digital computer and an almost completely automatic computational program, studies of the Created Response Surface Technique applied to the optimization of the hypothetical kraft pulping system were

made. The new approach was found to optimize the pulping system model in a very satisfactory manner. Adjustment of the operating variables provided improvements in net return of from $55,000 to $98,000 per year for the hypothetical systems studied. The main purpose of the optimization studies, however, was to investigate further the nature and use of the Created Response Surface Technique.

CONCLUSIONS

CONCLUSIONS CONCERNING THE OPERATIONS RESEARCH APPROACH APPLIED TO THE HYPOTHETICAL KRAFT PULPING SYSTEM

The Operations Research approach is a very effective approach to the economic optimization of the kraft pulping process considered in this thesis.

A suitable mathematical model of the system was developed (see Appendices III and IV) and its optimization efficiently accomplished (see Appendix VII). The quantitative results obtained in the optimization studies were highly characteristic of the hypothetical pulping system considered. These results were intended primarily to help explore further the nature and use of the Created Response Surface Technique, and to concretely illustrate the general nature of the Operations Research approach.

CONCLUSIONS CONCERNING THE PULPING RATE EXPRESSION*

1. It was possible to develop from fundamental considerations, and to experimentally verify a rather comprehensive rate expression interrelating the important kraft cooking variables in the pulping system studied. The form of the rate expression developed is expected to apply to other <u>similar</u> pulping systems provided the limitations mentioned below (2, 3, and 4) are not violated.

2. The rate expression for the system was tested for cooks in the 23-27.5 permanganate number range (40-ml. basis). It therefore applies with assurance only in this range.

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* See Appendix I.

3. The particular rate expression developed was for a straight line time-up-to-temperature schedule. Other time-temperature schedules could have been treated.

4. A significant limitation on the use of the expression seems to relate to the maintenance of reaction conditions characterized by sodium hydroxide as the rate-controlling constituent. Under such conditions, neither sulfidity nor molar concentration of sulfide were determining variables. Thus, they did not enter as such in the rate expression. Rather, it was active alkali which was found to be determining in the system studied.

5. The average concentration concept developed in this thesis is expected to be a useful concept in the development of other rate expressions and in characterizing cooking conditions.

6. Increasing the average concentration and increasing the liquor-to-wood ratio each decreased pulp yield when cooking to the same permanganate number, in the system studied.

7. The precision with which the experimental results verified virtually the same rate expression as the one theoretically developed lends credence to the validity of the assumptions and concepts in the development. However, in spite of this and the probable physical significance of several of the rate equation constants, the expression sould be considered as somewhat empirical. It is definitely not a kinetic expression capable of reliably predicting orders of reaction.

8. The developed and verified pulping rate expression provided an entirely suitable representation of the cooking operation for

the pulping system considered in the economic optimization of this thesis. In the optimization, though, it was assumed that the laboratory expression had been properly "scaled up" to mill conditions. Restraint R2 of the model and certain characteristics of the hypothetical pulping system provided that the hypothetical mill operation did not violate any of the limitations relating to the use of the rate expression.

9. Additional work, perhaps of a similar nature, will be necessary to quantitatively describe delignification rates over the full range of pulping conditions (especially the normal commercial range).

10. Some of the problems undoubtedly relating to past difficulty in developing comprehensive rate equations are: studying cooks over too large a range, both with respect to cooking conditions and degree of pulping; lack of quantitative consideration for changing chemical concentration during a cook; lack of a quantitative accounting for the time-up-to-temperature period; and failure to treat systems using shavings, sawdust, prehydrolysis treatments, etc., as possibly different from conventional systems using chips.

CONCLUSIONS CONCERNING THE CREATED RESPONSE SURFACE TECHNIQUE*

1. The Created Response Surface Technique (CRST) is, as far as is known, a new approach to the optimization of nonlinear, restrained systems.

2. The method was very effective in optimizing the hypothet-

* See Appendices V, VI, and especially VIII.

ical kraft pulping process in this thesis.

3. The CRST is expected to have broad applicability in optimizing general, complex, nonlinear, restrained systems. Such systems are very important industrially. In addition, the new approach may be of use in obtaining approximate optimum solutions in certain linear programming problems.

4. The observations and guide rules concerning the use of the CRST (see Appendix VIII) are expected to be of general utility even though they were derived from the limited experience of this thesis.

5. The CRST can be used in experimental designs for optimizing nonlinear, restrained systems just as the Method of Steepest Ascents has been used for optimizing nonlinear, unrestrained systems. The new approach can also be applied to "Evolutionary Operation" and automatic optimum control for nonlinear, restrained processes.

6. A practical and virtually automatic computer program for the CRST can be established. However, every optimization problem is different, and the particular characteristics of each must be taken into account in setting up an efficient computational procedure for solution. Automatic programs have special significance in automatic optimum control systems.

7. A modified use of the CRST, involving estimation of optimal conditions by an extrapolation procedure, holds promise of being an especially effective way of optimizing nonlinear, restrained systems. This would be particularly true in the experimental attainment of optimum

conditions where the model involved is only partially quantified.

8. Continued application of the CRST, in regular and modified form, to a wide variety of restrained optimization problems would provide additional experience needed in further interpretation and more efficient use of the new approach. Of particular interest is the mathematical nature (smoothness, continuity, shape, etc.) of the created response surfaces in relation to the effectiveness function, the restraints, and the penalty weighting factors involved.

SOME CONCLUSIONS CONCERNING THE APPLICATION OF THE OPERATIONS RESEARCH APPROACH TO OTHER KRAFT PULPING SYSTEMS

The mathematical model of the hypothetical kraft pulping system of this thesis is characterized, to a large extent, by many realistic assumptions, simplifications, and limitations. It is, nevertheless, still specific, and cannot be expected to serve as an exact prototype for the development of other pulping system models. The characteristics of every system must be determined separately. Indeed, another system may be comprised of entirely different equipment and include many different operations.

Furthermore, in extending the Operations Research approach to existing kraft pulping operations, there may arise a need for certain basic information which is currently not even available. For instance, consider the optimization of a bleached sulfate pulp mill operation. The development of sets of pulping rate expressions applying over the whole range of cooking conditions, the quantitative interrelationship of pulp quality characteristics and cooking conditions, and the development of kinetic expressions for bleaching reactions

would all be important contributions helping to make possible the application of the Operations Research approach. The problems to be solved before an application can be made to an entire integrated papermaking process are apparent.

In addition to problems of model formulation, the actual optimization of typical, industrially derived models may require the development of special techniques. For example, consider a nonlinear, restrained model of a stochastic process involving several sets of pulping rate equations each applying only over a given range of cooking conditions. Optimization of such a model presents problems which could, perhaps, be most efficiently met by the development of a new approach.

SOME CONCLUSIONS CONCERNING THE OPERATIONS RESEARCH APPROACH IN GENERAL

A very important contribution of Operations Research is the development of a reserved, yet confident, reliance on results of studies of isolated "subsystems." These subsystems--usually far too complex for intuition alone to comprehend--represent only a portion of the over-all system. Yet, developing even simplified subsystem models and obtaining appropriate solutions can uncover vastly improved operating conditions.

In addition, many important indirect benefits result. Some of these are:

1. The system is much better understood.
2. The cost of intuitive decisions and arbitrary management policies can be estimated.

3. Attention is focused on important variables and on where supplementary information may be required, where better control is desirable, where costs can be most easily reduced, where equipment "operating inferiority" is greatest, where bottlenecks occur, and where simplifications can be made in the model.

4. The development of a mathematical model allows interrelationships to be recorded so as not to be confusing or forgotten when another phase of the system is under study.

5. Models developed can usually be easily altered when the corresponding system changes due to temporary operating disruptions, cost and revenue changes, performance characteristic and equipment changes, changes in restraints, etc.

6. Models developed during suboptimization studies can be amalgamated to make a more comprehensive model, or can be elaborated upon to allow for a more inclusive or accurate subsystem description.

7. There can be justified confidence that answers obtained are correct; even if an optimization gives little or no improvement in effectiveness, this result can be relied upon, and study of another phase of the over-all system can be started without feeling the previous study was incomplete.

8. Sometimes new techniques of general utility are devised (e.g., the Created Response Surface Technique); or certain relationships, developed in the course of the study, find additional uses (e.g., the pulping rate expression and others like it can be used to simplify experimental designs and reduce the time and cost required for pulping research).

Finally, Operations Research can, in principle, be just as successfully applied to problems of design and replacement as to operating problems. The design considerations involved in the hypothetical pulping process model of this thesis were included to emphasize this point.

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APPENDIX I.

DEVELOPMENT, VERIFICATION, AND DISCUSSION OF A RATE EXPRESSION FOR KRAFT PULPING REACTIONS

NOTATION FOR APPENDIX I

A.A.	active alkali: NaOH + Na_2S each expressed as g. Na_2O
c	concentration of NaOH
c_{av}	average A.A. concentration (g./l.) according to Equation (43)
c'_{av}	average A.A. concentration (g./l.) according to Equation (39)
$(c_{av})_s$	average sulfide concentration according to Equation (46)
$(c'_{av})_s$	average sulfide concentration according to Equation (45)
c_i	initial A.A. concentration, g./l.
c_w	initial A.A.-to-wood ratio, g./g.
k, k', k'', k'''	constants related to chemical consumption
K no.	permanganate number, 40-ml. basis
L	% lignin in pulp at any time, t, based on original o.d. wood
L_f	final % lignin in pulp, based on original o.d. wood
L_i	initial % lignin in wood, based on o.d. wood
l/w	liquor-to-wood ratio, ml./g.
S	sulfidity: (g. Na_2S as Na_2O)100/A.A., %
T	temperature at any time, t, ^{o} abs. K
T_m	maximum temperature, ^{o} abs. K
T_o	initial temperature, ^{o} abs. K
t	time
t_t	total time of a cook, min.
t_u	time-up-to-temperature, min.
V_L	total liquor volume, ml.

$\underline{w}$	original o.d. wood charge, g.
$\underline{Y}$	total pulp yield, % o.d. pulp based on o.d. wood
α	constant related to sulfide consumption in Equation (46)
α_1	% "difficultly removed" lignin based on original o.d. wood
α_2'', α_2', α_2	apparent rate constants when NaOH is controlling
$(\alpha_2)_{\underline{S}}$	apparent rate constant when sulfide is controlling
α_3	constant related to apparent energy of activation for gross pulping reaction
α_4, α_5, α_6, α_7, α_8	constants related to A.A. consumption
$\alpha_{\underline{S}}$	constant related to sulfide consumption

DEVELOPMENT OF THE RATE EXPRESSION

The formulation of a pulping system model for this thesis required the development of a cooking rate expression for the production of an unbleached grade of spruce kraft pulp. It was necessary that the expression involve all the important kraft cooking variables over a reasonably wide range of cooking conditions.

For a given kraft pulping system, the cooking variables usually considered as important are: initial temperature ($\underline{T}_o$); time-up-to-temperature ($\underline{t}_u$); maximum temperature ($\underline{T}_m$); total time of cook ($\underline{t}_t$); sulfidity ($\underline{S}$); and two of: initial active alkali concentration ($\underline{c}_i$), initial active alkali-to-wood ratio ($\underline{c}_w$), and liquor-to-wood ratio ($\underline{l}/\underline{w}$). In addition, the time-temperature schedule during the cook must be known.

Kraft pulping studies (15) have been made where the concentration, c, of NaOH (presumed to be the rate-limiting constituent) has been held effectively constant during the reaction by means of very high chemical-to-wood ratios. These studies indicate that the "apparent" (16, 17) rate of delignification, when cooking at constant temperature and to yields corresponding to those for unbleached grades of pulp, can be represented by

$$\frac{dL}{dt} = \alpha_2'' c(L - \alpha_1), \qquad (1)$$

or

$$\frac{dL}{L - \alpha_1} = \alpha_2'' c \, dt \qquad (34)$$

where L represents the percentage lignin based on the original o.d. wood at any time, t. The constant, α_1, appears to represent "difficultly removed lignin" (15, 17-19). There may be some physical and/or chemical basis for this. In any case, α_1 allows for a better fit of the data.

The rate of delignification is, by Equation (1), proportional to the concentration, a phenomenon noted more or less qualitatively elsewhere (17, 19-21).

APPLICATION OF THE ARRHENIUS EQUATION

The α_2'' (the apparent rate constant) of Equations (1) and (34) depends on the temperature, T. The general applicability of the Arrhenius Equation to nearly all kinds of chemical reactions is well known (22). Many investigators have suggested or demonstrated the usefulness of the Arrhenius Equation to pulping reactions, e.g., (15,

17, 18, 20, 23). Vroom (23), in particular, has shown the broad applicability of this equation to kraft pulping reactions. While Vroom was not interested in absolute reaction rates, the Arrhenius Equation can be used to build into Equation (34) an appropriate time-temperature relationship, resulting in Equation (35):

$$\frac{dL}{L - \alpha_1} = \alpha_2'(e^{-\alpha_3/T})\, c\, dt. \qquad (35)$$

Here α_2' is the product of α_2'' of Equation (34) and the apparent "collision frequency factor" of the Arrhenius Equation. Constant α_3 is related to the apparent energy of activation for the gross pulping reaction.

Groups of cooks studied in Vroom's work can be considered as having varied only in temperature and time in reaching the same final degree of pulping. Therefore, chemical consumption, and thus average concentration during a given group of cooks, can be considered to have been effectively constant.

The integration of Equation (35) at constant concentration requires temperatures to be expressed as functions of time. If a cooking schedule is followed, this relationship is known; or it can be observed or predicted. In the hypothetical mill considered in this thesis, temperature rise is straight-line during the time-up period, and thereafter the temperature is constant. (See Figure 5.) The time-temperature relationships for these two periods are:

$$T = T_o + t(T_m - T_o)/t_u, \quad 0 \leq t \leq t_u, \qquad (36)$$

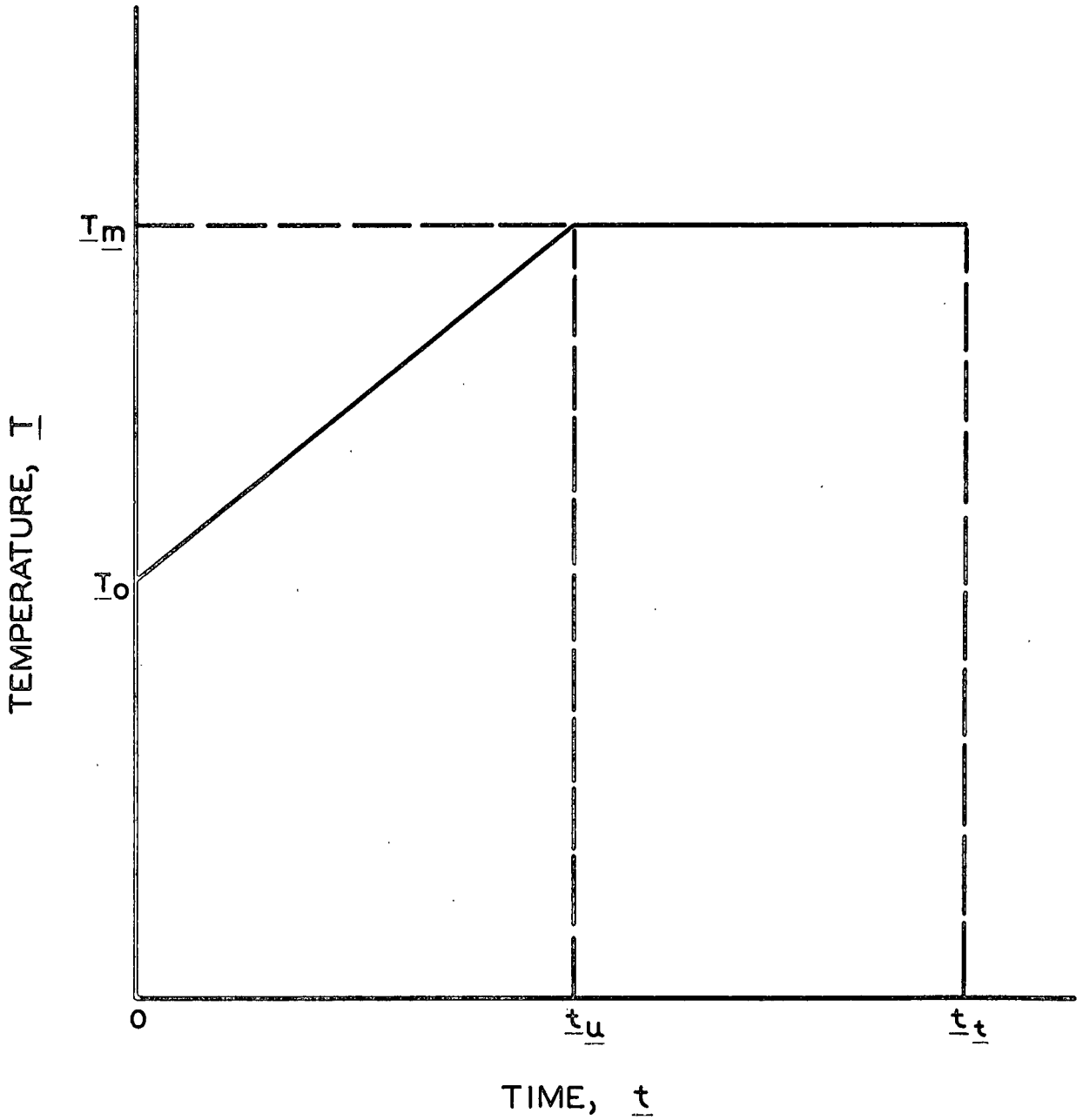

Figure 5. Temperature-Time Relationship in Hypothetical Mill

and

$$\underline{T} = \underline{T}_m, \qquad \underline{t}_u \leq \underline{t} \leq \underline{t}_t. \tag{37}$$

Equations (36) and (37) allow Equation (35) to be integrated at constant concentration.

VARIATION IN CONCENTRATION DURING THE COOK

For any industrially realistic kraft cooking operation, though, concentration varies significantly during the cook. This is because continuous consumption of cooking chemicals leaves noticeable deficits in the limited amounts of chemical which can be economically present. The concentration at any time during a cook depends not only on initial concentration, $\underline{c}_i$, and the chemical consumption, but also on $\underline{c}_w$, the chemical-to-wood ratio. The interrelationship between $\underline{c}_i$ and $\underline{c}_w$ has been repeatedly emphasized in connection with the qualitative concept of a "mean concentration" during a cook (19, 21, 24).

In order to apply Equation (35) to the industrially realistic situation of varying concentration, it is necessary to know how concentration changes with time or lignin content throughout a cook. From Hagglund and Hedlund's work (25), the lignin content of the pulp, $\underline{L}$, and from Borlew and Pascoe's work (26), the NaOH concentration, $\underline{c}$, can each be plotted, qualitatively, against time, $\underline{t}$, (Figure 6). Then NaOH concentration and pulp lignin content (or lignin dissolved) can be related by plotting one against the other at the same times (the curve in Figure 7).

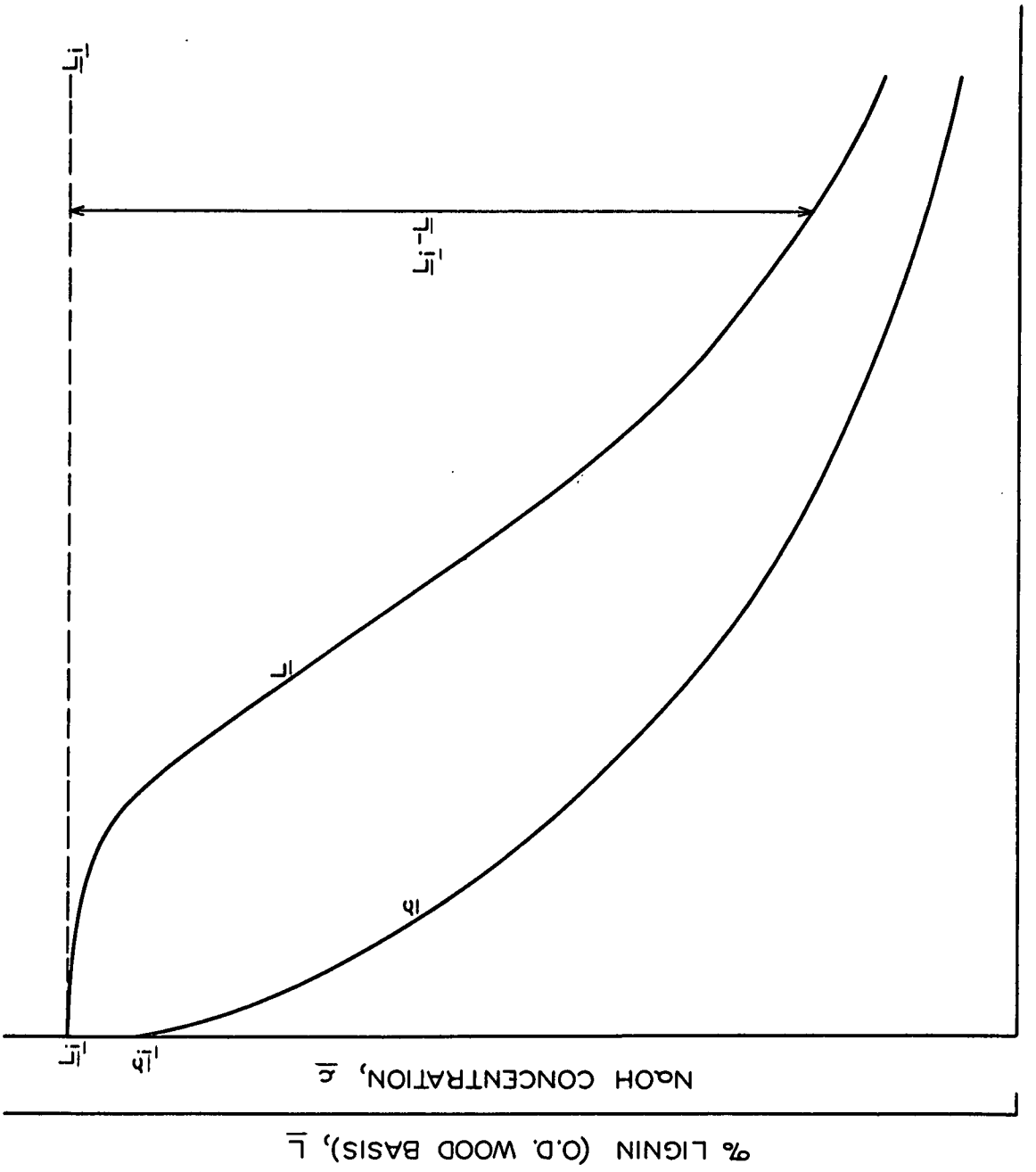

Figure 6. Qualitative Interrelationships Between NaOH Concentration and Time and Lignin and Time

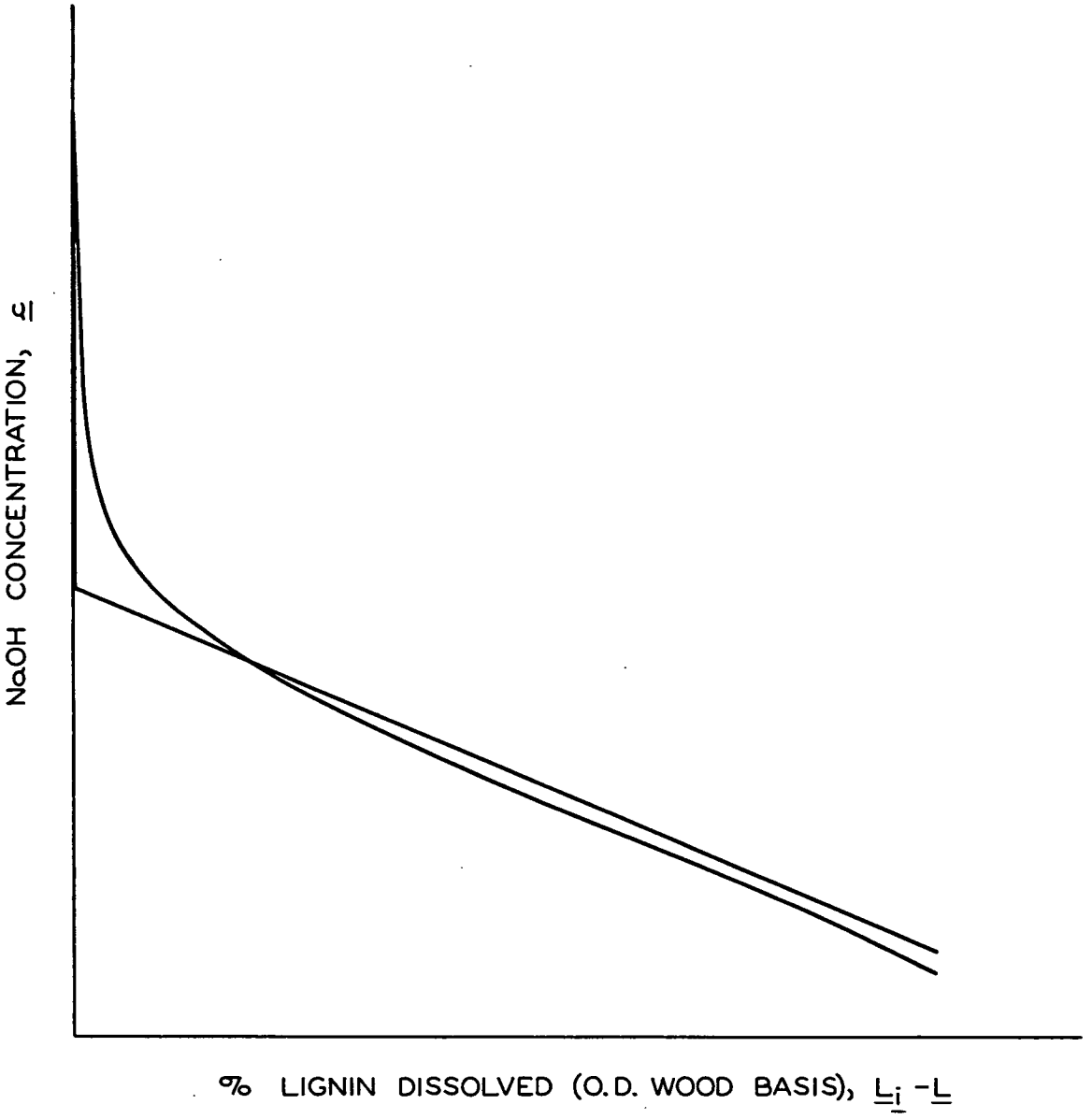

Figure 7. Qualitative Interrelationship Between NaOH Concentration and Lignin Dissolved (Curved line, actual, from Fig. 6; straight lines, approximate)

Initially, as has long been known, considerable NaOH is consumed almost immediately, due to extensive reaction with carbohydrates at temperatures at which lignin is almost unreactive. Thereafter, the decrease in NaOH slows and falls nearly linearly with the lignin remaining in the pulp. This is consistent with observations that NaOH consumption is directly proportional to wood dissolved (27), while wood dissolved is directly proportional to lignin dissolved (28) during this stage of soda cooks. [In Figure 7, lignin dissolved is $(\underline{L}_i - \underline{L})\underline{w}/100$, where $\underline{L}_i$ is the initial lignin content of the wood and $\underline{L}$ is the pulp lignin content at time, $\underline{t}$, each expressed as a percentage based on original o.d. wood weight. The o.d. wood charge is $\underline{w}$.]

Figure 7 shows that this typical change in NaOH concentration during delignification can be very well approximated by an initially large, immediate consumption of NaOH proportional to the carbohydrates (wood) present, $\alpha_{4\underline{w}}$, followed by a linear decrease (displaying some characteristic slope, α_5) as lignin is dissolved out of the pulp. Thus, concentration at any time during the cook can be expressed as

$$\underline{c} = \underline{c}_i - \frac{\alpha_4 \underline{w} + \alpha_5(\underline{L}_i - \underline{L})\underline{w}}{\underline{V}_L},$$

or

$$\underline{c} = \underline{c}_i - \frac{\underline{c}_i}{\underline{c}_w}[\alpha_4 + \alpha_5(\underline{L}_i - \underline{L})] \qquad (38)$$

where $\underline{V}_L$ is the total liquor volume.

Equation (38), along with Equations (36) and (37) can be substituted into Equation (35) and the latter then integrated (see final portion of Appendix II). However, a useful simplification can be made.

This is to consider an <u>average concentration</u>, $\underline{c'_{av}}$, which can be thought of as that concentration which, if maintained constant during the cook, would produce the same effects as a varying concentration initially at $\underline{c_i}$. The equation for $\underline{c'_{av}}$ has the same form as Equation (38) with $\underline{L}$ replaced by $\underline{L_f}$ (final pulp lignin content). But since all the cooks in the hypothetical mill considered in the economic optimization of this thesis are to the <u>same</u> final lignin content, the new equation defining $\underline{c'_{av}}$ can be written:

$$\underline{c'_{av}} = \underline{c_i} - \alpha_6 \frac{\underline{c_i}}{\underline{c_w}}. \qquad (39)$$

Equation (39) would be expected to be applicable over a limited range of $\underline{L_f}$ (or permanganate numbers) since the slope, α_5, in Equation (38) is probably relatively small (see Discussion).

THE INTEGRATED RATE EXPRESSION

Substituting Equation (39), along with Equations (36) and (37), into Equation (35) and integrating between appropriate limits using, where necessary, suitable approximations, one obtains:

$$\underline{t_t} = \frac{\ln \dfrac{\underline{L_f} - \alpha_1}{\underline{L_i} - \alpha_1}}{\alpha'_2 \left(\underline{e}^{-\alpha_3/\underline{T_m}} \right) \left(\underline{c_i} - \alpha_6 \dfrac{\underline{c_i}}{\underline{c_w}} \right)} + \underline{t_u} \left[1 - \frac{\underline{T_m}^2}{\alpha_3 (\underline{T_m} - \underline{T_o})} \right] \qquad (40)$$

The integration is developed in Appendix II. In the integration, $\underline{c'_{av}}$ is treated as a constant concentration since, under the conditions assumed, it depends only on initial conditions: $\underline{c_i}$ and $\underline{c_w}$ [see Equation (39)].

ESTIMATION OF $\underline{L_f}$ FROM $\underline{K}$ NO. AND $\underline{Y}$

The final pulp lignin content, $\underline{L_f}$, can be estimated from the permanganate number ($\underline{K}$ no.) and total unscreened pulp yield ($\underline{Y}$) by means of Equation (41):

$$\underline{L_f} = [(\underline{K}\text{ no.})(0.292) - 2.53]\frac{\underline{Y}}{100}. \qquad (41)$$

This equation was derived by combining Borlew and Keller's work (29) showing a general linear relationship between Roe chlorine number and lignin content,[a] and a linear approximation based on Hart and Strapp's data (31), wherein $\underline{K}$ no. and Roe chlorine number can be related for spruce pulp cooked to a $\underline{K}$ no. of around 25.[b] (This is the kind of pulp considered in the economic optimization.)

Substituting Equation (41) into Equation (40) gives

$$\underline{t_t} = \frac{\ln \dfrac{[(\underline{K}\text{ no.})(0.292) - 2.53]\dfrac{\underline{Y}}{100} - \alpha_1}{\underline{L_i} - \alpha_1}}{\alpha_2\left(e^{-\alpha_3/\underline{T_m}}\right)\left(\underline{c_i} - \alpha_6\dfrac{\underline{c_i}}{\underline{c_w}}\right)} + \underline{t_u}\left[1 - \frac{\left(\underline{T_m}\right)^2}{\alpha_3\left(\underline{T_m} - \underline{T_o}\right)}\right]. \qquad (42)$$

Equation (42) was tested with certain of Hart and Strapp's comprehensive kraft pulping data (31). In their work, the sulfidity was constant at 33% while the liquor-to-wood ratio was fixed at 3.5 ml./g. Time-temperature relationships were straight-line and known. There was evidence

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[a] $\underline{L_f}$ = [(0.811)(Roe chlorine number) - 0.110]$\underline{Y}$/100; a similar expression derived recently for spruce appears in (30).

[b] Roe chlorine number = 0.360($\underline{K}$ no.) - 2.98.

enough that with very careful control and sufficient data, Equation (42) might well prove to be the integrated rate expression desired. However, experimental results would, in addition to verifying Equation (42), have to indicate how sulfidity (or the concept of "effective alkali") might be incorporated. Consequently, a laboratory investigation was undertaken with these purposes in mind.

EXPERIMENTAL VERIFICATION OF THE RATE EQUATION

A number of carefully controlled cooks were made under conditions designed to verify Equation (42) and to provide information as to how sulfidity might be incorporated. The experimental design involved the following ranges of cooking variables:

$\underline{l}/\underline{w}$, ml./g.	6.736-15.459
$\underline{c}_{\underline{i}}$, g. A.A./l.	26.72-57.90
$\underline{c}_{\underline{w}}$, g. A.A./g.	0.1800-0.6885
$\underline{S}$, %	25.0-60.0
Na_2S conc., mol/l.	14.22-46.69
Max. temp., ^{o}C.	160 and 170
Init. temp., ^{o}C.	31.0-35.0
$\underline{t}_{\underline{u}}$, min.	60 and 90

EXPERIMENTAL PROCEDURE

A sufficient amount of sprucewood was collected from the woodyard of the Interlake Division of Consolidated Water Power & Paper Co., Appleton, Wisconsin. This wood was then chipped in The Institute of Paper Chemistry chipper, and the chips, after being mixed thoroughly, were moisture-sampled while a large number of storage bags were

progressively filled with a given wet (and therefore o.d.) weight of chips. The bags of chips were stored in a cold room until immediately before use.

The active cooking chemicals used were commercial flake NaOH and "purified crystals" of Na_2S. Solutions of each of these basic kraft cooking chemicals were made up periodically, stored separately, and frequently titrated so as to monitor any chemical change. The NaOH (and Na_2CO_3) concentrations were determined in triplicate by the standard HCl double end-point titration, using phenolphthalein and methyl orange indicators. Only a trace of Na_2CO_3 was ever present. The Na_2S concentration was determined in quadruplicate by TAPPI Standard T 624 m-44, modified by using slightly different aliquots and a constant 10 ml. of 4 $\underline{N}$ H_2SO_4 in place of acetic acid. It was assumed that sulfite and thiosulfate were present in only negligible amounts.

Immediately before a given cook, required amounts of each stock solution were drawn off, mixed, and diluted to the desired total volume, $\underline{V_L}$. The desired active alkali concentration ($\underline{c_i}$) and sulfidity were obtained by considering the stock solution concentrations, the o.d. wood charge ($\underline{w}$), the required liquor-to-wood ratio, and the water present in the chips. In order to provide initial chip coverage when the basket of chips was in position in the digester, a liquor-to-wood ratio [$\underline{V_L}$(ml.)/$\underline{w}$(g.)] of at least about 6.7 ml./g. was required.

The chips, which were 85.80% dry, were cooked in a basket in a conventional, indirect-heated, laboratory digester. Very rigid temperture-time control was maintained during the cooks. A typical temperature-time record is shown in Figure 8. Virtually complete relief was

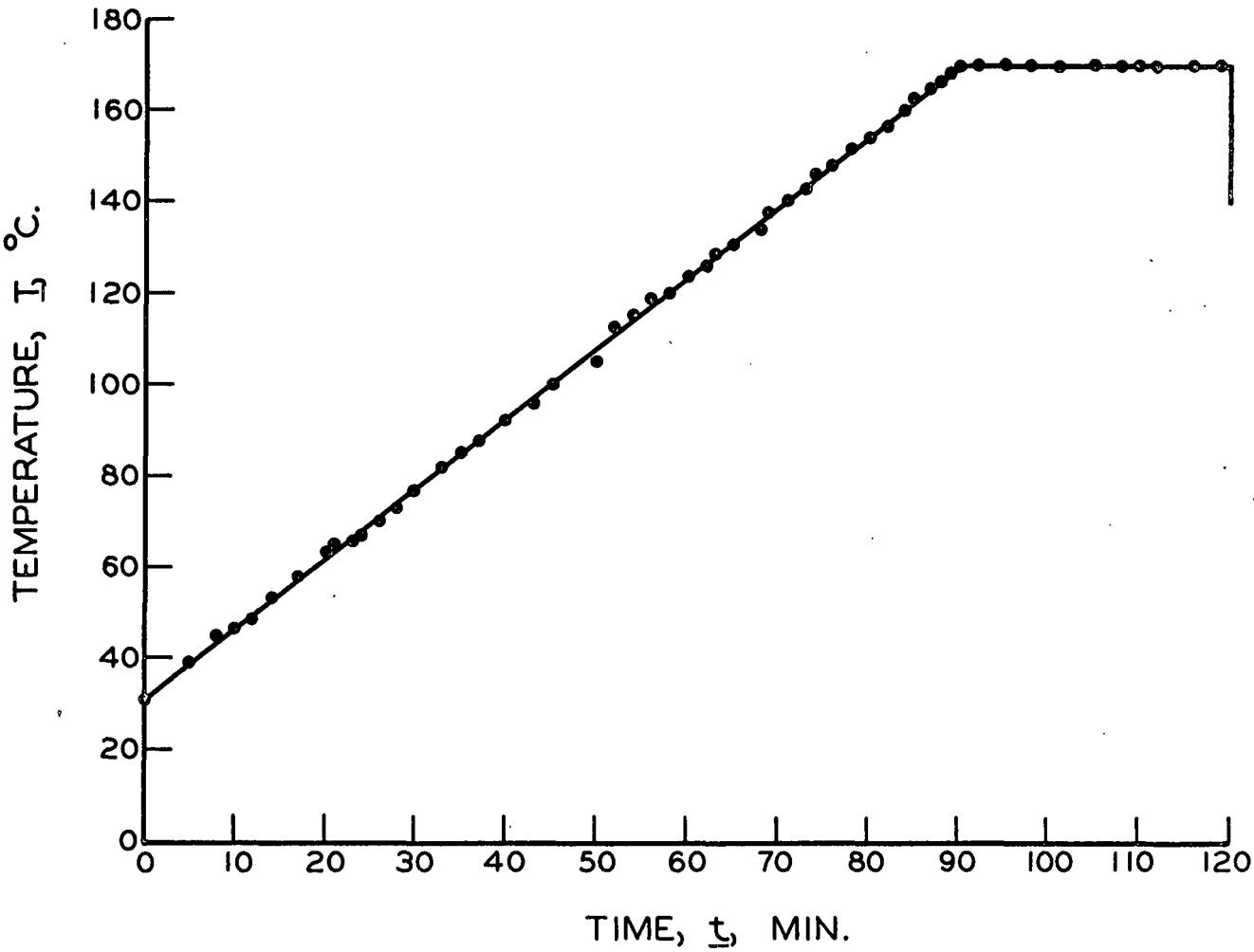

Figure 8. Typical Temperature-Time Data for Experimental Cooks

provided at 100°C. and the digester was blown at full pressure. The blow was accomplished in a matter of seconds. The temperature of the chip mass dropped to below 120°C. in less than half a minute following a blow. During the cook, the temperature read was that of the liquor stream coming into the top of the digester from the heat exchanger.

The hot pulp was brush-refined (at a "loose" 0.003 inch) in a Sprout-Waldron laboratory refiner to provide good disintegration of the pulped chips with a minimum of mechanical damage to the fibers. The refined pulp was then thoroughly washed and centrifuged. Yields were determined in quadruplicate. Yield moisture samples were oven dried in a 105°C. oven for two days. The standard deviation of yield determinations was about 0.13%.

Following yield determination, a representative portion of the pulp was screened (screenings were negligible) in preparation for permanganate number determination. An improved sampling technique allowed for considerably increased precision and accuracy in the permanganate number procedure. This improved technique involved the simultaneous filling of seven 1000-ml. graduate cylinders each with a slurry volume expected to give (based on duplicate consistency samples) 1 g. o.d. pulp. Permanganate numbers were determined on four of these samples, randomly chosen, by use of the analytical procedure described in TAPPI Standard T 214 m-50. A 40-ml. basis was always used. The remaining three samples were used to estimate the o.d. weight of pulp actually present in the permanganate number determinations. The standard deviation in K no. determinations was about 0.26, much better than could have been obtained using the conventional sampling technique with the same equipment.

DATA AND RESULTS

The experimental data and calculated results are shown in Table I. Preliminary calculations indicated that for a good fit of the data, the expression for $\underline{c}'_{av}$ [Equation (39)] needed the addition of an apparently empirical constant, α_8, representing additional chemical consumption. For generality, the value of α_6 in Equation (39) was replaced by a new constant, α_7. Equation (39) thus became Equation (43):

$$\underline{c}_{av} = \underline{c}_i - \alpha_7 \frac{\underline{c}_i}{\underline{c}_w} - \alpha_8 \ .* \qquad (43)$$

Using Equation (43) instead of Equation (39), Equation (42) becomes Equation (44):

$$\underline{t}_t = \frac{\ln \dfrac{[(\underline{K}\text{ no.})(0.292) - 2.53]\dfrac{\underline{Y}}{100} - \alpha_1}{\underline{L}_i - \alpha_1}}{\alpha'_2\left(\underline{e}^{-\alpha_3/\underline{T}_m}\right)\left(\underline{c}_i - \alpha_7 \dfrac{\underline{c}_i}{\underline{c}_w} - \alpha_8\right)} + \underline{t}_u\left[1 - \frac{(\underline{T}_m)^2}{\alpha_3(\underline{T}_m - \underline{T}_o)}\right] \qquad (44)$$

The values of "Calc. $\underline{t}_t$" in Table I were derived by use of Equation (2), below. Equation (2) is Equation (44) with "best-fit" values for the undetermined constants, along with the yield and $\underline{K}$ no. actually occurring in the cooks. The initial lignin content of the wood, $\underline{L}_i$, is taken to be 26% for the spruce chips used (see "Constants in the Rate Expression" in the Discussion). In effect, "Calc. $\underline{t}_t$" is "$\underline{t}_t$ predicted" for the particular conditions and the expected yield and $\underline{K}$ no. Equation (2),

* Note: A $\underline{c}_{av}$ giving virtually as good a fit as Equation (43) could have been expressed by other functional forms, such as $\underline{c}_i - \gamma_1(\underline{c}_i/\underline{c}_w)^{\gamma_2}$ where γ_1 and γ_2 are "best-fit" constants. However, these seem no less empirical than Equation (43). Consequently, Equation (43) was used.

TABLE I
EXPERIMENTAL DATA AND CALCULATED RESULTS FOR KRAFT PULPING RATE EXPRESSION

Cook	l/w, ml./g.	c_i, g. A.A./l.	c_w, g. A.A./g.	S, %	Na_2S Conc., mol/l.	Max. Temp., °C.	Init. Temp., °C.	t_u, min.	Y, %	K no.	L_f [a]	-ln [b]	e [c]	t [d]	c_{av} [e]	Calc. t_t, min.	Act. t_t, min.	Δ [f]	% Error [g]
9	6.736	31.18	0.2100	33.0	.1659	170.0	33.0	90.0	49.5	24.9	2.35	2.920	38.74	82.0	16.28	170.7	171.7	-1.0	-0.58
8	6.736	35.63	0.2400	33.0	.1896	170.0	33.0	90.0	48.9	24.4	2.24	3.002	38.74	82.0	20.73	153.6	153.1	0.5	0.33
3	6.736	40.09	0.2700	33.0	.2134	170.0	35.0	90.0	48.4	25.8	2.42	2.870	38.74	81.9	25.19	138.2	138.0	0.2	0.14
18	6.736	40.09	0.2700	33.0	.2134	170.0	34.0	90.0	48.8	25.1	2.34	2.926	38.74	81.9	25.19	139.3	140.1	-0.8	-0.57
6	6.736	44.54	0.3000	33.0	.2371	170.0	32.0	90.0	48.3	24.8	2.29	2.968	38.74	82.1	29.64	131.6	131.5	0.1	0.08
5	6.736	48.99	0.3300	33.0	.2608	170.0	34.0	90.0	48.4	25.3	2.36	2.915	38.74	81.9	34.09	124.2	124.8	-0.6	-0.48
7	6.736	53.45	0.3600	33.0	.2845	170.0	31.0	90.0	48.1	25.0	2.29	2.963	38.74	82.1	38.55	120.1	119.9	0.2	0.17
4	6.736	57.90	0.3900	33.0	.3082	170.0	31.0	90.0	48.0	25.3	2.34	2.927	38.74	82.1	43.00	115.8	115.6	0.2	0.17
12	6.736	48.99	0.3300	40.0	.3161	170.0	34.0	90.0	48.6	23.9	2.16	3.067	38.74	81.9	34.09	126.4	126.8	-0.4	-0.32
13	6.736	35.63	0.2400	60.0	.3448	170.0	34.0	90.0	49.1	22.9	2.05	3.172	38.74	81.9	20.73	157.6	157.1	0.5	0.32
14	6.736	57.90	0.3900	50.0	.4669	160.0	34.0	60.0	48.8	24.7	2.28	2.969	16.74	54.5	43.00	133.5	132.5	1.0	0.76
20	15.459	44.54	0.6885	33.0	.2371	170.0	33.0	90.0	47.5	25.5	2.33	2.934	38.74	82.0	35.20	123.2	123.6	-0.4	-0.32
21	15.459	31.18	0.4820	33.0	.1659	170.0	33.0	90.0	48.1	25.0	2.29	2.962	38.74	82.0	21.84	149.1	148.7	0.4	0.27
22	11.092	40.09	0.4447	33.0	.2134	170.0	33.0	90.0	47.9	24.7	2.24	3.000	38.74	82.0	29.06	133.0	132.8	0.2	0.15
15	15.459	44.54	0.6885	33.0	.2371	170.0	33.0	90.0	47.6	27.3	2.59	2.758	38.74	82.0	35.20	120.7	120.4	0.3	0.25
16	15.459	44.54	0.6885	33.0	.2371	170.0	33.0	90.0	47.6	27.6	2.63	2.728	38.74	82.0	35.20	120.3	120.4	-0.1	-0.08
19	15.459	44.54	0.6885	33.0	.2371	170.0	33.0	90.0	48.1	27.2	2.60	2.748	38.74	82.0	35.20	120.6	120.4	0.2	0.17
10	6.736	26.72	0.1800	33.0	.1422	170.0	35.0	90.0	50.0	26.2	2.56	2.772	38.74	81.9	11.82	197.9	204.7	-6.8	-3.32 [h]
11	6.736	48.99	0.3300	25.0	.1976	170.0	34.0	90.0	49.2	29.5	3.00	2.528	38.74	81.9	34.09	118.6	122.9	-4.3	-3.50 [h]

[a] $L_f = [(K \text{ no.})(0.292) - 2.53](Y/100)$, %

[b] $-ln = -\ln[(L_f - 1.00)/25.00]$

[c] $e = e^{40.00 - (16{,}100/T_m)}$, T_m, ° abs.

[d] $t = t_u\left[1 - \frac{T_m^2}{16{,}100(T_m - T_o)}\right]$, T_m and T_o, ° abs.

[e] $c_{av} = c_i - (0.0663)(c_i/c_w) - 5.05$

[f] Δ = Calc. t_t - Act. t_t, min.

[g] % Error = (100)Δ/Act. t_t

[h] These significantly higher negative errors indicate a different and slower reaction rate than that in the other cooks. (See the Discussion.)

used to derive "Calc. t_t" in Table I, is:

$$t_t = \frac{\ln \dfrac{[(K \text{ no.})(0.292) - 2.53]\dfrac{Y}{100} - 1.00}{25.00}}{\left(-5.22 \times 10^{-5}\right)\left(e^{40.00 - (16{,}100/T_m)}\right)\left(c_i - (0.0663)\dfrac{c_i}{c_w} - 5.05\right)}$$

$$+ t_u\left[1 - \frac{(T_m)^2}{16{,}100(T_m - T_o)}\right]. \qquad (2)$$

The $e^{40.00}$ is inserted for convenience in calculation. Thus,

$$-5.22 \times 10^{-5} = (e^{40.00})\alpha_2' = \alpha_2,$$

the apparent rate constant for Equation (2).

Equation (2) precisely defines the interrelationship of the cooking variables for the system studied under certain broad limitations on the values of a few of the variables. (These limitations and the absence of sulfidity or effective alkali in the rate equation are discussed in the next section.) An idea of the reproducibility possible may be obtained by comparing Cooks 15, 16, and 19--all replicates of the same set of cooking conditions. The standard deviation determined on all cooks (except Cooks 10 and 11--see Discussion below) is 30 seconds. The 95% confidence limits on "Calc. t_t" are about ± 1.0 minute. This corresponds to a maximum error of $\pm 0.88\%$. The average deviation of "calculated" from "actual" t_t, regardless of sign, is about 25 seconds, corresponding to a maximum error of 0.31%.

DISCUSSION

ABSENCE OF SULFIDITY IN THE RATE EXPRESSION

It is at first startling that sulfidity or some measure of sulfide concentration is not included as such in the integrated rate expression [Equation (2)]. This is because sulfidity above 33% or, more significantly, sulfide expressed in terms of molar concentration (which covers about a threefold range--see Table I) is not a determining variable in the system studied. Rather, it is active alkali regardless of its composition (sulfidity) which is important. (However, see the minimal sulfide requirement discussed under "Limitations Applying to the Rate Expression.")

This situation might be explained by assuming that essentially all the Na_2S hydrolyzes to NaHS and NaOH, and that virtually all of the NaHS thus formed immediately hydrolyzes further to H_2S and more NaOH. (Since, by this hypothesis, essentially all the sodium present eventually ends up in the form of NaOH, the initial, potential molar concentration of NaOH is approximately proportional to the active alkali concentration, c_i. Thus, either can be used to express initial NaOH concentration in the system studied. Of course, because of a difference in units, the value of the apparent rate constant, α_2, in each case would be different.) The hypothesized H_2S resulting from a virtually complete hydrolysis of Na_2S could possibly form an activated complex with the lignin and allow for easier removal by NaOH than is the case in the soda process. The possibility of H_2S being an active cooking chemical in kraft pulping has been expressed elsewhere [see, e.g., (32)].

APPLICATION OF THE RATE EXPRESSION

Equation (2) is directly applicable only to the specific system described in the experimental procedure. That is, the particular "best-fit" constants appearing in Equation (2) are characteristic of this system alone, provided close control is maintained during the cooks and the limitations discussed below (also characteristics of the system) are met. Certain of the constants may have more fundamental significance and be more "universal" than others; however, this is only speculation. (In this connection, see the discussion section on constants.) Thus, application of the general form of Equation (2) to another similar system implies that the constants must be determined by analysis of data taken under carefully controlled conditions wherein the limitations mentioned below are not violated.

LIMITATIONS APPLYING TO THE RATE EXPRESSION

For the system studied, certain limitations apply to the use of Equation (2) and thus to the mathematical model for which it was developed. The values of c_i, c_w, and sulfidity must be such that a condition of "limiting sulfide" is avoided. In Cooks 10 and 11, possibly Na_2S (or a derivative of it, e.g., H_2S) rather than NaOH (presumed to be rate controlling in the other cooks) was the component reacting at the limiting rate because of its presence in insufficient amounts. This resulted in a K no. higher than that which is predicted by Equation (2). Such an outcome is to be expected and is consistent with recent literature concerning a limiting sulfide concept [see, e.g., (33)].

Apparently, a condition of limiting sulfide is avoided, for the system studied, by maintaining the following conditions:

$$\underline{c_i} \geq 31.18 \text{ g./l.}$$

$$\text{liquor-to-wood ratio} = (\underline{c_w}/\underline{c_i})1000 \geq 6.736 \text{ ml./g.}$$

$$\text{sulfidity} = \frac{(Na_2S)100}{NaOH + Na_2S} \geq 33$$

Another limitation applying to Equation (2) is that the volume of liquor circulated must be sufficient to preclude "channeling." Also, the equation has not been tested outside of the 23-27.5 K no. range (40-ml. basis) and, consequently, should be used beyond this range only with due reserve.

Still another limitation involves the temperature-time schedule. Equation (2) has been developed and thus holds for a straight-line rise up to maximum temperature, $\underline{T_m}$, which is then maintained constant. Other temperature-time relationships could be incorporated by integrating (perhaps graphically, or in a tabular manner [see (23)]) the appropriate function in the derivation of the rate expression.

CONSTANTS IN THE RATE EXPRESSION

Equation (2) was derived and presumably gains much of its precision from incorporation of certain, more or less, fundamental concepts. It must, nevertheless, be looked upon as an empirical rate expression. The following, for example, underscore this empirical nature: the greater utility of Equation (44) compared to Equation (62) of Appendix II; the greater utility of Equation (43) than Equation (39) due to the inclusion of an empirical, additional consumption factor, α_8;

and the empirical manner whereby pulp lignin is estimated from K no. (see discussion below). In addition, for the system and limitations involved, Equation (2) predicts the specific results or outcome of cooks characterized by pulps having a K no. in a given range. The expression does not (nor was it developed to) describe accurately the course and accompanying characteristics of the reaction. Thus, in general, kinetic interpretation of Equation (2) is somewhat risky.

In spite of the empirical nature of Equation (2), the "best-fit" values of certain of the constants may be of interest if not of theoretical significance. For instance, the residual lignin content, α_1 [Equation (2) is very sensitive to changes in α_1], has the value, 1.00, corresponding to 1% "unavailable" or "difficultly removed" lignin. This value is consistent with Kulkarni and Nolan's work (15) and the observations of others [e.g., (17) and (18)]. No doubt, the value of α_1 is actually dependent upon the K no. range to which the cooks are made [see, e.g., (16)].

The apparent rate constant, α_2 (= -5.22×10^{-5}), compares fairly closely with that found in the preliminary studies based on Hart and Strapp's data (31). Their study was of a presumably similar system (however, see the next section). The value of α_2 for a given rate-limiting condition is probably highly characteristic of the system. Thus, the type of wood, its moisture content, the nature of the chips, the size of the digester, final yield range, etc. all influence α_2.

A value of 16,100 was used for α_3 (related to the apparent heat of activation for the gross reaction). This value was found to be satisfactory in Vroom's work (23). Since Equation (2) is not too sensitive to

α_3, and since α_3 relates to the gross reaction, the particular value of 16,100 must be considered empirical.

Constants α_4, α_5, α_7, and α_8 relate to chemical consumption. For certain of Hart and Strapp's data, an α_4 of 0.085 and α_5 of 0.001 appeared to be "best-fit" values in the 50% yield and 25 K no. range. The value of L_i was 25.97 and a best-fit α_1 seemed to be 1.00. Substituting these values into the chemical consumption portion of Equation (38), it is seen that consumption, when cooking to the yield range involved, was $[0.085 + 0.001(25.97 - 1.00)]100 \cong 11\%$ based on the o.d. wood charge. This is quantitatively consistent with the 12% chemical charge often considered to be the minimum necessary in pulping for defibering satisfactorily to 50% yield in the slower soda process (27). The quantitative significance of constant α_7 and α_8 in Equations (43) and (44) of the present work is unknown.

Finally, the quantitative significance of the constants (0.292 and 2.53) in Equations (41) and (2) relating final pulp lignin content, L_f, to K no., is also unknown. This is because the lignin which is reactive to pulping chemicals in the digester under the severe reaction conditions there is probably not the same lignin which is reactive at room temperature to $KMnO_4$ in the K no. determination. The initial wood lignin content, L_i, as measured by conventional wood lignin procedures, is also related in an unknown manner to the lignin reactive under cooking conditions. Because of this, and because the initial lignin content of sprucewood probably varies less than the range over which L_i could vary without important consequences to the fitting of the experimental results,

L_i was not actually determined, but was set at a typical value: 26%. (Recall that Hart and Strapp's spruce (31) was 25.97% lignin.) Thus, L_i can be looked upon as a characteristic of the system rather than literally as the initial reactive lignin content of the wood. In this connection, the important point is that through proper adjustment of constants, Equation (2) accurately predicts the outcome of allowable cooks. The utility of Equation (2) is its primary justification.

A RATE EXPRESSION WHERE SULFIDE IS LIMITING

Sulfide may be rate limiting at the start of a cook or become so during a cook. In developing rate equations for such situations, it is important to be able to express concentration of sulfide at any time during the cook. In the development of such an expression, not only the initial concentration of sulfide but also sulfide consumption and initial sulfide charge must be considered. This is analogous to the considerations involving changing NaOH concentration leading up to Equation (38).

Only Cooks 10 and 11 are apparently in the range where sulfide is rate controlling, at least part of the time. These two cooks do not supply nearly enough information to determine the nature of the rate expression in this range. A complete experimental design based as fully as possible on the expected form of such a rate expression is required for this situation just as it was when, presumably, NaOH was limiting. Such an experimental program might be designed to determine or verify the apparent order of reacting constituents and the various constants appearing in the differential form of a rate expression. The resulting expression could then give insight into mechanisms, perhaps shedding light

on the validity of an "effective alkali" concept, the importance of hydrosulfide and hydrolysis, etc.

In spite of the inadequacy of the data from the present study for determining the nature of a rate expression where sulfide is limiting, the results of Cooks 10 and 11 can, perhaps, be used in a preliminary investigation of the general nature of such an expression, and in further interpretation of Hart and Strapp's work (31).

Assume that for cooks under conditions such as those for Cooks 10 and 11, sulfide is the only rate-limiting constituent and that the reaction between sulfide (e.g., H_2S) and lignin is of the same nature as that supposedly occurring between the hypothesized complexed lignin and NaOH. In addition, assume that the new α_3 (very probably different from the appropriate α_3 applying when NaOH is the rate-determining constituent) affects the second term on the right of Equation (2) only negligibly and that its effect on the $\underline{e}^{40.00 - \alpha_3/\underline{T}_m}$ term is absorbed in the apparent rate constant. Assume further that the average sulfide concentration, $(\underline{c}'_{av})_{\underline{S}}$, can be written in a manner analogous to $\underline{c}'_{av}$ expressed by Equation (39). Thus,

$$(\underline{c}'_{av})_{\underline{S}} = \underline{c}_{\underline{i}} \frac{\underline{S}}{100} - \alpha_{\underline{S}} \frac{\underline{c}_{\underline{i}}}{\underline{c}_{\underline{w}}}. \qquad (45)$$

where $\underline{c}_{\underline{i}}(\underline{S}/100)$ is the initial sulfide concentration and $\alpha_{\underline{S}}$ is a constant; the sulfidity is $\underline{S}$.

If $\underline{c}_{av}$ of Equation (2) is replaced by this expression for $(\underline{c}'_{av})_{\underline{S}}$, then the cooking conditions and results of the two cooks, 10 and

11, can be used to determine two constants: e.g., $\alpha_{\underline{s}}$ and a new apparent rate constant, $(\alpha_2)_{\underline{s}}$. When this is done,

$$\alpha_{\underline{s}} = 0.0461$$

and

$$(\alpha_2)_{\underline{s}} = -2.93 \times 10^{-4}.$$

It is known that sulfide concentration decreases some, but not excessively, during typical cooks (26). When, however, typical conditions are considered, for example,

$$\left.\begin{aligned} \underline{S} &= 25\% \\ \underline{c_i} &= 50 \text{ g./l.} \\ \underline{c_w} &= .18 \end{aligned}\right\} \underline{l/w} = 3.6 \text{ ml./g.},$$

the consumption portion of Equation (45), $\alpha_{\underline{s}}(\underline{c_i}/\underline{c_w})$, is so large that negative $(\underline{c'_{av}})_{\underline{s}}$ values result. Even zero values indicate infinite cooking times.

Thus, it can be cautiously concluded that if sulfide is, indeed, the rate-limiting constituent in Cooks 10 and 11, and if the data of Cooks 10 and 11 are accurate, then $(\underline{c'_{av}})_{\underline{s}}$ as expressed by Equation (45) is too small. Perhaps average sulfide concentration is better represented by some other function, possibly of the form,

$$(\underline{c_{av}})_{\underline{s}} = \underline{c_i}\,\frac{\underline{S}}{100} - \alpha f(\underline{c_i}/\underline{c_w}), \qquad (46)$$

where α is a constant and f is a function of $\underline{c_i}/\underline{c_w}$ [i.e., f is essentially a function of the liquor-to-wood ratio = $(\underline{c_w}/\underline{c_i})1000$].

It is interesting to note here that if Equation (46) is of the correct form when sulfide is limiting, then one cannot really tell what the true rate-limiting factor or factors are in Hart and Strapp's work (31). (See the concluding remarks of the "Development of the Rate Expression" section of this appendix.) This is because their study was at constant sulfidity and constant liquor-to-wood ratio, and under these conditions, Equation (46) becomes

$$(\underline{c}_{av})_{\underline{s}} = \underline{k}\underline{c}_{\underline{i}} - \underline{k}'$$

or

$$\frac{1}{\underline{k}} (\underline{c}_{av})_{\underline{s}} = \underline{c}_{\underline{i}} - \underline{k}''. \qquad (47)$$

Equation (43) for a constant liquor-to-wood ratio becomes

$$\underline{c}_{av} = \underline{c}_{\underline{i}} - \alpha_7 \frac{\underline{c}_{\underline{i}}}{\underline{c}_{\underline{w}}} - \alpha_8 = \underline{c}_{\underline{i}} - \underline{k}'''. \qquad (48)$$

Equation (48) has the same form as Equation (47) above. The $1/\underline{k}$ of Equation (47) can be absorbed by the apparent rate constant, $(\alpha_2)_{\underline{s}}$. In a similar manner, any interpretation in terms of an effective alkali concept becomes confused.

PROBLEMS IN DEVELOPING RATE EXPRESSIONS

The discussion so far may shed some light on certain problems which have possibly precluded an earlier development of a comprehensive pulping rate expression. Studying pulping reactions over too wide a range, both with respect to the cooking variables and the degree of pulping, has perhaps been the greatest impediment. Such studies involve such a variety of reaction conditions, it is likely that a number

of rate-controlling factors are involved in the removal of a given constituent. Such a situation may prevail not only from cook to cook but also during a given cook. A single rate expression (continuous in the first derivative and lacking "easement" features) cannot be expected to be useful under these conditions. In addition, due to the complexity of wood and, consequently, of the reactions in which it is involved, only a correspondingly complex set of rate expressions could predict a gross phenomenon such as yield as a function of time throughout the entire cook [see, for example, (16)].

Other factors contributing to past difficulty in developing useful rate expressions include: failure to account for concentration changes during the cook; lack of quantitative consideration for the time-up-to-temperature period; inadequate temperature-time control; and failure to treat systems using shavings, sawdust, prehydrolysis treatments, etc. as possibly different from conventional systems using chips.

USE OF RATE EXPRESSIONS

Other laboratory-derived pulping rate expressions can be used, like the one in this thesis, in pulping process optimization studies. It should be noted that, in this application, "scale-up" from laboratory to mill is an important part of the problem.

Another potentially important use of rate expressions is in minimizing the work required in experimental pulping investigations. Having an applicable pulping rate expression, pulping experimentation could be limited to the accurate determination of the rate-expression constants, and a few check cooks to verify the predictability of the equation. The desirability of ultimately being able to express pulp

quality characteristics, as well as the degree of pulping, as functions (similar in nature to the rate expressions) of the cooking conditions, is apparent. Then, all the desired pulping information for the system could be calculated, once the characteristic constants of the system are determined.

YIELD AS A FUNCTION OF AVERAGE CONCENTRATION

The effect of concentration on yield is often evaluated in pulping studies. The following can be concluded from the experimental results for the system studied (see Table I):

1. For a given average concentration, yield probably decreases insignificantly with a reduction (by means of longer cooks) in final K no. in the 23-27.5 range. Thus, any concentration effect on yield would seem to come mainly earlier in a cook. (Compare Cooks 15, 16, 19, and 20.)

2. When cooking to a given K no. range (23-25.7) and at a given liquor-to-wood ratio, yield decreases significantly, as $\underline{c}_{av}$ increases. Thus, $\underline{Y}$ = 49.5 for $\underline{c}_{av}$ = 16.28; $\underline{Y}$ = 48.0 for $\underline{c}_{av}$ = 43.00. (The standard deviation for $\underline{Y}$ is about 0.13%).

3. When cooking to a given K no. range (23-25.7), increasing the liquor-to-wood ratio at a given $\underline{c}_{av}$ probably decreases yield (compare Cooks 20, 21, and 22 with Cooks 5, 8, and 6, respectively.)

CONCLUSIONS

The conclusions from this portion of the thesis are included in the section, Conclusions (page 34), in the body of the thesis.

APPENDIX II.

INTEGRATION OF THE DIFFERENTIAL RATE EXPRESSION DEVELOPED IN APPENDIX I

This appendix describes the integration of Equation (35) in Appendix I for the case where:

(1) time-up-to-temperature is a straight line [see Equations (36) and (37)], and

(2) concentration is $\underline{c}'_{av}$, given by Equation (39), and constant so far as the integration is concerned, since $\underline{c}'_{av}$ depends only on initial conditions ($\underline{c}_i$, $\underline{c}_w$).

That is, this appendix shows the integration of

$$\frac{d\underline{L}}{\underline{L} - \alpha_1} = \alpha'_2(e^{-\alpha_3/\underline{T}})\,\underline{c}\,d\underline{t} \qquad (35)$$

where

$$\underline{T} = \underline{T}_o + \underline{t}(\underline{T}_m - \underline{T}_o)/\underline{t}_u, \quad 0 \leq \underline{t} \leq \underline{t}_u; \qquad (36)$$

$$\underline{T} = \underline{T}_m, \quad \underline{t}_u \leq \underline{t} \leq \underline{t}_t; \qquad (37)$$

$$\underline{c} = \underline{c}'_{av} = \underline{c}_i - \alpha_6(\underline{c}_i/\underline{c}_w) = \text{constant}; \qquad (39)$$

and

$\underline{L}$ goes from $\underline{L}_i$ to $\underline{L}_f$;

$\underline{T}$ goes from $\underline{T}_o$ to $\underline{T}_m$;

$\underline{t}$ goes from 0 to $\underline{t}_t$ $(\geq \underline{t}_u)$.

The result of the integration is Equation (40) of Appendix I.

THE INTEGRATION GIVING EQUATION (40)

Equation (35) may be rewritten:

$$\frac{dL}{\alpha'_2\ c(L - \alpha_1)} = (e^{-\alpha_3/T})\ dt \qquad (49)$$

Substituting $c = c'_{av}$ (a constant), indicating integration of both sides over the designated range, and substituting appropriately for T, Equation (49) becomes

$$\frac{1}{\alpha'_2\ c'_{av}} \int_{L_i}^{L_f} \frac{dL}{L - \alpha_1} = \int_{0}^{t_u} e^{-\alpha_3/(T_o + t(T_m - T_o)/t_u)}\ dt +$$

$$\int_{t_u}^{t_t} e^{-\alpha_3/T_m}\ dt. \qquad (50)$$

The quantity on the left can be integrated to give

$$\frac{\ln \dfrac{L_f - \alpha_1}{L_i - \alpha_1}}{\alpha'_2\ c'_{av}}. \qquad (51)$$

The second integral on the right becomes

$$(t_t - t_u)e^{-\alpha_3/T_m}. \qquad (52)$$

The first integral on the right-hand side of Equation (50),

$$\int_{0}^{t_u} e^{-\alpha_3/(T_o + t(T_m - T_o)/t_u)}\ dt, \qquad (53)$$

requires substitution and approximation for its determination. The integration of Expression (53) follows. Let

$$\underline{x} = \frac{\alpha_3}{\underline{T_o} + \underline{t}\,\dfrac{\underline{T_m} - \underline{T_o}}{\underline{t_u}}} .$$

Thus,

$$\underline{t} = \frac{\alpha_3\,\underline{t_u}}{\underline{x}(\underline{T_m} - \underline{T_o})} - \frac{\underline{T_o}\,\underline{t_u}}{\underline{T_m} - \underline{T_o}} ;$$

$$d\underline{t} = - \frac{\alpha_3\,\underline{t_u}}{\underline{T_m} - \underline{T_o}} \frac{d\underline{x}}{\underline{x}^2} .$$

When

$$\underline{t} = 0, \ \underline{x} = \alpha_3/\underline{T_o} ;$$

and when

$$\underline{t} = \underline{t_u}, \quad \underline{x} = \alpha_3/\underline{T_m} .$$

In terms of $\underline{x}$, the integral (53) thus becomes

$$- \frac{\alpha_3\,\underline{t_u}}{\underline{T_m} - \underline{T_o}} \int_{\alpha_3/\underline{T_o}}^{\alpha_3/\underline{T_m}} \underline{e}^{-\underline{x}}\, d\underline{x}/\underline{x}^2 \tag{54}$$

$$= \frac{\alpha_3\,\underline{t_u}}{\underline{T_m} - \underline{T_o}} \left[\int_{\alpha_3/\underline{T_m}}^{\infty} \underline{e}^{-\underline{x}}\, d\underline{x}/\underline{x}^2 - \int_{\alpha_3/\underline{T_o}}^{\infty} \underline{e}^{-\underline{x}}\, d\underline{x}/\underline{x}^2 \right] \tag{55}$$

$$< \frac{\alpha_3 t_u}{T_m - T_o} \left[\left(\frac{T_m}{\alpha_3} \right)^2 \int_{\alpha_3/T_m}^{\infty} e^{-x}\, dx - \left(\frac{T_o}{\alpha_3} \right)^2 \int_{\alpha_3/T_o}^{\infty} e^{-x}\, dx \right] \quad (56)$$

$$= \frac{\alpha_3 t_u}{T_m - T_o} \left[\left(\frac{T_m}{\alpha_3} \right)^2 e^{-\alpha_3/T_m} - \left(\frac{T_o}{\alpha_3} \right)^2 e^{-\alpha_3/T_o} \right]. \quad (57)$$

For values of T_o and T_m characteristic of typical cooks, the second term in Equation (57) is negligible compared to the first. Thus, Equation (57) becomes, approximately:

$$\frac{(T_m)^2 t_u e^{-\alpha_3/T_m}}{\alpha_3 (T_m - T_o)} . \quad (58)$$

However, each of the terms in Equations (56) and (57), and the expression (58), is an approximation, being slightly larger than the corresponding terms in Equation (55). The error in approximating Equation (54) by Equation (58) is, essentially, that due to approximating the first term of Equation (55) by the first term of Equation (56) [which, when integrated, becomes Equation (58)]. Thus:

$$\text{error} = \frac{\alpha_3 t_u}{T_m - T_o} \int_{\alpha_3/T_m}^{\infty} \left[\frac{1}{(\alpha_3/T_m)^2} - \frac{1}{x^2} \right] e^{-x}\, dx$$

$$= \frac{\alpha_3 t_u}{T_m - T_o} \int_{\alpha_3/T_m}^{\infty} \left[\frac{x^2 - (\alpha_3/T_m)^2}{(\alpha_3/T_m)^2 x^2} \right] e^{-x}\, dx$$

$$< \frac{\alpha_3 t_u}{T_m - T_o} \left(\frac{T_m}{\alpha_3}\right)^4 \int_{\alpha_3/T_m}^{\infty} [x^2 - (\alpha_3/T_m)^2]\, e^{-x}\, dx$$

$$= \frac{(T_m)^4 t_u}{(T_m - T_o)(\alpha_3)^3} \left\{ -e^{-x} [x^2 - (\alpha_3/T_m)^2 + 2x + 2] \right\}_{\alpha_3/T_m}^{\infty}$$

$$= \frac{2(T_m)^4 t_u}{(T_m - T_o)(\alpha_3)^3} \left[e^{-\alpha_3/T_m} (\alpha_3/T_m + 1) \right]. \qquad (59)$$

Since $\alpha_3/T_m \gg 1$ (e.g., $\alpha_3 = 16{,}100$ and $T_m = 443$),

Equation (59) becomes Equation (60):

$$\text{error} \cong \frac{2(T_m)^3 t_u e^{-\alpha_3/T_m}}{(T_m - T_o)(\alpha_3)^2}. \qquad (60)$$

Therefore, % error in the approximation of Equation (53) by Equation (58) is, about,

$$\frac{[\text{Eq. (60)}]\,100}{\text{Eq. (58)} - \text{Eq. (60)}} = \frac{200\, T_m}{\alpha_3 - 2T_m}.$$

For $T_m = 443^\circ$ abs. (170°C.)

and $\alpha_3 = 16{,}100$,

$$\% \text{ error} = 5.8\%.$$

This error is not very "temperature sensitive"; for 160°C., the error is 5.7%, and for 180°C., it is 6.0%. Thus, Equation (58) is, essentially, a consistently large approximation for Equation (54) and its equivalent,

Equation (53). The use of Equation (58) implies, then, that the "apparent rate constant," α_2', will be consistently smaller than the "true" α_2'.

By combining Equations (51), (52), and (58), the complete integrated form of Equation (49) [equivalent to Equation (35) of the text] becomes:

$$\frac{\ln \dfrac{L_f - \alpha_1}{L_i - \alpha_1}}{\alpha_2' \, c'_{av}} = \frac{(T_m)^2 \, t_u \, e^{-\alpha_3/T_m}}{\alpha_3(T_m - T_o)} + (t_t - t_u)e^{-\alpha_3/T_m}, \qquad (61)$$

or, solving Equation (61) for t_t and substituting $c'_{av} = c_i - \alpha_6 \dfrac{c_i}{c_w}$, Equation (40) of Appendix I results:

$$t_t = \frac{\ln \dfrac{L_f - \alpha_1}{L_i - \alpha_1}}{\alpha_2'\left(e^{-\alpha_3/T_m}\right)\left(c_i - \alpha_6 \dfrac{c_i}{c_w}\right)} + t_u\left[1 - \frac{T_m^2}{\alpha_3(T_m - T_o)}\right]. \qquad (40)$$

This is the desired result.

THE INTEGRATION USING EQUATION (38)

Equation (49) [essentially Equation (35)] can be integrated using Equation (38) of Appendix I as an expression for c:

$$c = c_i - \frac{c_i}{c_w}\left[\alpha_4 + \alpha_5 (L_i - L)\right]. \qquad (38)$$

In this case, the left-hand side of Equation (49) may be integrated by partial fractions. The other integrals remain the same. The resultant

expression for $\underline{t}_{\underline{t}}$ is:

$$\underline{t}_{\underline{t}} = \frac{\ln \dfrac{\underline{L}_f - \alpha_1}{\underline{L}_i - \alpha_1} - \ln \dfrac{\underline{c}_w - [\alpha_4 + \alpha_5(\underline{L}_i - \underline{L}_f)]}{\underline{c}_w - \alpha_4}}{\left(\alpha'_2 \, \underline{e}^{-\alpha_3/\underline{T}_m}\right)\left(\underline{c}_i - \dfrac{\underline{c}_i}{\underline{c}_w}[\alpha_4 + \alpha_5(\underline{L}_i - \alpha_1)]\right)} + \underline{t}_u \left[1 - \frac{(\underline{T}_m)^2}{\alpha_3 \underline{T}_m - \underline{T}_o}\right]. \tag{62}$$

It might be expected that Equation (62) would apply even more generally than Equation (44) and be useful over larger $\underline{K}$ no. ($\underline{L}_f$) ranges. This does not seem to be the case when applied to actual experimental data from this work. Thus, while Equation (62) can probably cope with a wider $\underline{L}_f$ range, the concentration terms lack a counterpart to the "additional consumption" factor, α_8, of Equation (44).* Perhaps by redefining Equation (38) so as to include such an additional consumption factor, and then integrating Equation (35) again, as in this appendix, a more flexible rate expression could be developed.

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* Note: Equation (62), with suitable substitution for $\underline{L}_f$, approaches a limit different from that of Equation (44), as $\underline{c}_w \rightarrow \infty$. This difference is due to the additional consumption factor, α_8.

APPENDIX III.

DEVELOPMENT OF MATERIAL, ENERGY, AND ECONOMIC BALANCES FOR A BASE CASE

INTRODUCTION

The purpose of this appendix is to develop material and energy balances, revenues, costs, and net return (the measure of effectiveness) based on an arbitrary, but realistic, particular set of operating conditions for the hypothetical pulping system. This base case facilitates the development of a generalized mathematical model (see Appendix IV). Specific quantities developed were also used in the model or validity check portion of the computer program. (See Appendix VII.)

The general nature of the hypothetical system is illustrated in Figure 2. Figure 3 is a detailed flow diagram of the hypothetical pulping process indicating the quantitative results of the base case engineering balances as developed in this appendix.

The starting point for the base case material balance will be a typical strong black liquor from the evaporators just before it enters the recovery boiler unit. First, the expected changes in material composition of this black liquor brought about in the recovery furnace will be developed. (The energy balances for the whole cycle are worked out following the over-all material balance.) Salt cake make-up is added to the furnace in an amount necessary to exactly offset system losses. Some inorganic loss occurs from the furnace stacks, but most of the inorganic chemicals entering undergo chemical and physical changes and become smelt (molten inorganic salts--mainly Na_2CO_3 and Na_2S). This smelt is the recovered chemical (plus make-up minus stack losses) which, upon dissolu-

tion in aqueous solution and conversion in the causticizing operation, becomes the white liquor for the cooking operation. It is necessary to determine the composition of the smelt so as to determine causticizing efficiency and thus the amounts of the various cooking chemicals present. In turn, the quantities of the cooking chemicals and the volume of the cooking liquor in the digester influence the rate of pulping.

In the cooking operation, white liquor and black liquor are mixed together with the chips and heated in the digesters. At the end of the cooking cycle, the resulting pulp and black liquor are transferred to a blowtank and thence to washers. Depending on the amount of fresh wash water used, more or less black liquor is lost with the pulp separated in the washing operation. This represents an inorganic chemical and potential heat loss, and creates a foam problem in the pulp screening operation.

The black liquor washed from the pulp at the washers, now diluted somewhat, is in part recirculated to the digesters. The remainder goes to the evaporators which concentrate it sufficiently for steady, self-sustained burning in the recovery furnace, and the cycle is completed.

The energy balances are dependent upon the material balances. High-pressure steam is generated in the boiler from the heat liberated by burning the organic matter of the black liquor solids (BLS). This steam is expanded through turbines which generate electricity. The turbines are designed so that some of the steam is "bled off" at an intermediate pressure for use primarily at the digesters. The remainder expands further to a lower pressure for use primarily at the evaporators. The electricity generated by the turbogenerator, and the

excess low-pressure steam, represent revenues, or "profits," from the operation.

The costs of concern are variable costs. They include the cost of salt cake and lime make-up; cost of defoamer; cost of lime kiln fuel; and cost of capital recovery, plus interest, for evaporators large enough to do the required evaporation. Note that this last cost is not a variable cost for the mill in operation, but is for the mill in contemplation by the designer.

The difference between revenues and variable costs is net return, and this is the measure chosen to express how effectively the system is operating.

Finally, certain realistic restraints will be brought in and quantitatively expressed during the course of the material balance. Some of these restraints (e.g., equipment and operating limitations) are necessarily imposed on the system. Others (e.g., policy limitations) are internal to a given company and somewhat arbitrary. Still others (e.g., customer specifications and legal requirements) are imposed on the system by the external environment.

NOMENCLATURE FOR APPENDIX III

BL	=	black liquor
BLS	=	black liquor solids
$\underline{C_e}$	=	installed cost of evaporators, dollars
$\underline{C_p}$	=	consistency of pulp off last washer, %
$\underline{c_i}$	=	initial active alkali concentration, lb./cu. ft.
$\underline{c_w}$	=	initial active alkali-to-wood ratio, lb./lb.

$\underline{D}$ = dilution factor, lb. H_2O/lb. air-dried pulp

$\underline{E}$ = measure of effectiveness (net return), dollars/TADP

$\underline{G}$ = rate of fresh wash water to washers, g.p.m.

$\underline{H}$ = heat in gross high-pressure steam generated, B.t.u./TADP

$\underline{I}$ = "water equivalent" of digester and contents, lb./TADP

$\underline{K}$, $\underline{k}$ = constants

$\underline{K}$ no. = permanganate number

$\underline{\ell}$ = BLS load to furnace, lb./TADP

$\underline{L_N}$ = unadjusted soda loss (as Na_2SO_4) from washers, lb./TADP

$\underline{M}$ = salt cake make-up (as Na_2O), lb./TADP

$\underline{n}$ = number of digesters

$\underline{Q}$ = quantity of pulp produced per digester charge, TADP

$\underline{R}$ = daily requirement of screened pulp, TADP

$\underline{R_i}$ = restraints

$\underline{s}$ = weight fraction solids in BL to evaporators and BL recirculated to digesters, lb./lb.

$\underline{S.E.}$ = steam economy, lb. H_2O evaporated/lb. steam

sp. $gr._{BL}$ = specific gravity of black liquor

sp. $gr._{WL}$ = specific gravity of white liquor

sp. $ht._{BL}$ = specific heat of black liquor

sp. $ht._{WL}$ = specific heat of white liquor

TADP = ton air-dried pulp

$\underline{t_b}$ = time between cooks, min.

$\underline{t_t}$ = total time for a cook, min.

$\underline{V_{BL}}$ = volume of BL to digesters, cu. ft./TADP

$\underline{V_D}$ = digester volume, cu. ft.

$\underline{V_L}$ = total volume of BL, WL, and moisture in chips, cu. ft./TADP

$\underline{V}_{WL}$ = volume of WL to digesters, cu. ft./TADP

$\underline{w}$ = o.d. wood charge, lb./TADP

WL = white liquor

$\underline{X}1$ = NaOH as Na_2O in WL before WL losses, lb./TADP

$\underline{X}2$ = Na_2S as Na_2O in WL before WL losses, lb./TADP

$\underline{X}3$ = Na_2SO_4 as Na_2O in WL before WL losses, lb./TADP

$\underline{X}4$ = Na_2CO_3 as Na_2O in WL before WL losses, lb./TADP

$\Sigma\underline{X}$ = total load of inorganic chemical as Na_2O in WL before WL losses, lb./TADP

$\Sigma\underline{X}_a$ = actual weight of total load of inorganic chemicals in WL before losses, lb./TADP

$\Sigma\underline{X}_s$ = actual weight of smelt from recovery furnace unit, lb./TADP

THE BASE MATERIAL BALANCE[a]

FURNACE[b]

A typical ultimate analysis of 1 lb. BLS from the evaporators is shown in Table II:

TABLE II

actual	Na_2O	Na	S	O_2	C	H_2	N_2
1.0000	0.2496	0.1852	0.0397	0.3136	0.4190	0.0407	0.0018

This composition closely approximates typical ones in the experience of Combustion Engineering, Inc. (35). Suppose that the above composition results when the amount of black liquor solids (BLS) per TADP is 2970 lb.

---

[a] Basis = lb. per ton of air-dried pulp (lb./TADP), unless otherwise stated.

[b] Patterned after the general development in (34).

The ultimate analysis of this 2970 lb. BLS is shown in Table III:

TABLE III

actual	Na_2O	Na	S	O_2	C	H_2	N_2
2970	741.3	550.0	117.9	931.4	1244.4	120.9	5.4

These 2970 lb. BLS enter the furnace. Fundamental to any calculation of material changes in the furnace is an estimation of the sulfur loss in the flue gases. It will be assumed here that 94%[a] of the total sulfur is retained in the smelt as Na_2SO_4 and the remaining Na present is combined as Na_2CO_3--before addition of salt cake, before fume loss, and before reduction (34). Table IV indicates the composition of this smelt (before addition of salt cake, before fume loss, and before reduction):

TABLE IV

Component	Na_2O, lb.	S, lb.	O_2, lb.	C, lb.
Na_2SO_4	214.7	110.8	221.6	--
Na_2CO_3	526.6	--	407.7	101.9
Total	741.3	110.8	629.3	101.9

Next, M lb. of salt cake (assumed 100% Na_2SO_4 and expressed as Na_2O) is added to the furnace (per TADP). In this base case, M is assumed to be 19.3 lb. This makes up for assumed losses (each expressed as lb. Na_2O/TADP) of 8.3 lb. in the fume, 7 lb. in the incompletely washed pulp, and 4 lb. from the causticizing operation. These losses can be considered fairly typical [see (34)]. Other losses are neglected.

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[a] However, see final portion of Appendix IV.

Maximum tolerable fume loss (see restraint R1), because of assumed air pollution legislation, will be considered to be K_1 lb./TADP. The value of K_1 is taken to be 10.0 in this base case and the generalized model.

Table V shows the composition of the smelt after addition of salt cake and after fume loss, but before reduction:

TABLE V

Component	Na_2O, lb.	O_2, lb.
Na_2SO_4	225.7	233.0
Na_2CO_3	526.6	407.7
Total	752.3	640.7

Now, assuming 95% reduction of Na_2SO_4 to Na_2S, the composition of the smelt becomes as in Table VI:

TABLE VI

Component	Actual, lb.	Na_2O, lb.	O_2, lb.
Na_2SO_4	25.9	11.3	11.7
Na_2S	269.7	214.4	--
Na_2CO_3	900.3	526.6	407.7
Total	1195.9 = ΣX_S	752.3 = ΣX	419.4

The weight of inorganic chemical in the smelt (expressed as Na_2O) is defined as ΣX, while the actual weight of the smelt is ΣX_S.

The O_2 released during reduction = 640.7 - 419.4 = 221.3.

The black-liquor-derived flue gas composition (not including O_2

released during reduction) can be obtained by subtracting from the total ultimate analysis of each BLS element (see Table III) the corresponding elemental value from Table IV. Table VII indicates the results:

TABLE VII

	Total From Ultimate Analysis of BLS, lb.	In Smelt, Before Addition of Salt Cake, Before Fume Loss, Before Reduction, lb.	Black-Liquor-Derived Flue Gas Minus O_2 Derived From Reduction
C	1244.4	101.9	1142.5
H_2	120.9	0.0	120.9
S	117.9	110.8	7.1
O_2	931.4	629.3	302.1
N_2	5.4	0.0	5.4

This composition of the black-liquor-derived flue gas will be used later in the energy balance.

CAUSTICIZING AND LIME KILN OPERATIONS (34, 36)

Causticizing Operation

The smelt from the furnace runs into the dissolving tank to become green liquor, which contains the unaltered chemical from the smelt. Since the Na_2CO_3 is probably inert in the cooking operation, it is desirable to convert it as completely as practicable to NaOH by causticization: $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$. The degree of completeness possible from this causticization reaction depends, primarily, upon the concentrations of the chemical components present. It also depends in the industrial case on the design of the equipment. Usually the operation is about 5% below maximum theoretical causticizing efficiency, defined as the equilibrium value of $100[NaOH]/([NaOH] + [Na_2CO_3])$, where

the brackets indicate concentrations.

Assuming an actual causticizing efficiency of 95% of the theoretical value, the experimentally developed equation of Hughey, Herndon, and Withrow (37) can be written:

$$\left(\frac{\underline{X1}}{\underline{X1} + \underline{X4}}\right)100 = 95.0 - [(4.782)(10^{-2})(\Sigma\underline{X} - \underline{X3}) + (1.956)(10^{-1})(\Sigma\underline{X} - \underline{X3})^2/$$

$$\underline{V}_{WL} + (6.376)(10^{-1})\underline{X2} + (1.594)\underline{X3}]\frac{1}{\underline{V}_{WL}} \qquad (63)$$

where

$\underline{X1}$ = lb. NaOH as Na_2O in the white liquor before losses/TADP,

$\underline{X2}$ = lb. Na_2S as Na_2O in the white liquor before losses/TADP,

$\underline{X3}$ = lb. Na_2SO_4 as Na_2O in the white liquor before losses/TADP,

$\underline{X4}$ = lb. Na_2CO_3 as Na_2O in the white liquor before losses/TADP,

(These are the only inorganic chemicals considered present.)

$\Sigma\underline{X} = \underline{X1} + \underline{X2} + \underline{X3} + \underline{X4}$, and

$\underline{V}_{WL}$ = volume of white liquor after losses, cu. ft./TADP[a].

Equation (19) of the model is Equation (63) rearranged and written with $\Sigma\underline{X} = \underline{Y1}$ and $\underline{V}_{WL} = \underline{Y2}$.

All the dilution water necessary to make the white liquor is added in the causticizing operation. The amount of water added here, and thus the white liquor volume, will depend on the effect of concentration on causticizing efficiency, lime recovery costs, and cooking kinetics, and the effect on the use of black liquor as a diluent in the digester, the cost of eventual evaporation of the water introduced, etc. More

[a] Equation (63) involves a factor of 0.995 so that $\underline{V}_{WL}$ (white liquor volume after losses of about 0.5%) can be used. See concluding remarks in this section.

concentrated white liquor means lower causticizing efficiencies, accompanied, however, by less evaporation or, perhaps, the use of more recirculated black liquor, or more wash water (with attendant decrease in BLS loss at the washers). But, the stronger the white liquor, the heavier the load of inert Na_2CO_3 in the system for a given strength of cooking chemicals, and the greater the soda losses. This influences salt cake input and thus the sulfidity, but this latter, if $\sim$ 25-33% or above, is probably of relatively minor importance of itself in pulping for the system considered (see discussion of rate expression in Appendix I).

Using the causticizing efficiency relationship of Equation (63); observing from Table VI that $\underline{X}2 = 214.4$ and $\underline{X}3 = 11.3$, while $\Sigma\underline{X} = 752.3$; and assuming $\underline{V}_{WL} = 124.3$; Table VIII indicates the composition of the inorganic chemical in the white liquor following causticization:

TABLE VIII

Component	Actual, lb.	Na_2O, lb.
NaOH	587.7	$\underline{X}1 = 455.5$
Na_2S	269.7	$\underline{X}2 = 214.4$
Na_2SO_4	25.9	$\underline{X}3 = 11.3$
Na_2CO_3	121.6	$\underline{X}4 = 71.1$
Total	$\Sigma\underline{X}_a = 1004.9$	$\Sigma\underline{X} = 752.3$

Note that the sulfidity, $\frac{\underline{X}2}{\underline{X}1 + \underline{X}2}(100) = 32.0\%$, or $\frac{\underline{X}2}{\underline{X}1 + \underline{X}2} = 0.32$. It is assumed that in order to avoid a condition of "limiting sulfide" (see discussion, Appendix I) in the subsequent cooking operation, it is

only necessary to maintain the sulfidity above 28%, i.e.:

$$\frac{X2}{X1 + X2} \geq K_2$$

where $K_2 = 0.28$. Restraint R2 in Exhibit I therefore assures the applicability of the pulping rate expression of Appendix I (and thus the model in which it is used) to the hypothetical pulping system considered.

The $\leq X_a$ is the actual weight of inorganic chemical in the white liquor (per TADP) before taking account of white liquor losses in the causticizing operation.

Chemical losses from the white liquor system are small (36, 38), and a 4.0-lb. loss (as Na_2O) ($\sim$0.5%) would typify good operation in the present situation. Since the loss is as white liquor, the concentrations remain unchanged.

Lime Recovery Cycle

Before turning to the cooking operation, the lime recovery cycle must be considered since the amount of lime required and thus lime losses (make-up) and B.t.u. consumption (cost) of the lime kiln operation are directly proportional to the NaOH produced in the causticizing operation (34).

1. Lime required (lb./TADP):

X1 = NaOH required (as Na_2O),

equivalent CaO = $\frac{56}{62}$ X1.

at 90% availability,

$$\text{equivalent impure lime} = \frac{56}{62}\,\frac{\underline{X}1}{0.90}\,.$$

Let additional lime requirements due to losses, unconverted lime, etc. be 10% of the equivalent impure lime. Then

$$\text{total impure lime required} = 1.10\,\frac{56}{62}\,\frac{\underline{X}1}{0.90}\,.$$

2. Lime make-up (lb./TADP):

assume lime losses = 4% of total impure lime required

Then,

$$\text{lime make-up (quicklime, CaO)} = 0.04\left[1.10\,\frac{56}{62}\,\frac{\underline{X}1}{0.90}\right].$$

3. Mud produced (lb./TADP):

$$\text{total available lime} = 1.10\,\frac{56}{62}\,\underline{X}1.$$

equivalent $CaCO_3$, assuming 2% of total available lime is unconverted:

(1) $$\text{total converted lime} = 0.98\left[1.10\,\frac{56}{62}\,\underline{X}1\right]\,\frac{100}{56}\,.$$

(2) $$\text{unconverted lime} = 0.02\left[1.10\,\frac{56}{62}\,\underline{X}1\right].$$

(3) $$\text{inert material} = \frac{0.10}{0.90}\left[1.10\,\frac{56}{62}\,\underline{X}1\right].$$

$$\text{total dry mud produced} = (1) + (2) + (3) =$$

$$\left[1.10\,\frac{56}{62}\,\underline{X}1\right]\left[0.98\,\frac{100}{56} + 0.02 + \frac{0.10}{0.90}\right].$$

When $\underline{X}1 = 455.5$,

$$\text{total dry mud produced} = 851.3.$$

Since the Na_2O loss is 4.0 lb., % loss is

$$(4.0/851.3)100 = 0.47\% < 0.50\%,$$

often considered a maximum for good operation.

4. B.t.u. required/TADP: Assume that the sludge to the kiln is always 40% moisture and that its heat requirement is 9×10^6 B.t.u./ton o.d. lime produced. Assuming the lime loss is made up by adding CaO (quicklime) and the loss up the kiln stacks is negligible compared with the accuracy of the heat requirement figure:

$$\text{ton o.d. lime produced/TADP} = \text{total impure lime required} - \text{lime make-up} = \frac{0.96}{2000}\left[1.10\,\frac{56}{62}\,\frac{X1}{0.90}\right].$$

Therefore, B.t.u. required =

$$9 \times 10 \times \frac{0.96}{2000}\left[1.10\,\frac{56}{62}\,\frac{X1}{0.90}\right].$$

The above expressions are used later in this appendix and in Appendix IV.

DIGESTER OPERATION (34, 39)

In the hypothetical mill, there are n vertical, stationary digesters, each indirectly heated and each having a capacity of 2700 cu. ft. $= V_D$. The daily production is to be 250 TADP with negligible yield loss in screening. Permanganate number (K no.) is fixed at 25.0 (unbleached grade of pulp). Pulp yield is constant at 47.4%. It is assumed that the physical properties and K no. of the pulp are independent of the cooking conditions employed to arrive at this fixed yield.

At a yield of 47.4%, the o.d. wood charge/TADP $= w = 3798$ lb. Let the specific heat of the o.d. wood $\doteq 0.33$. Assume the wood's moisture content (based on wet wood) to be 40%. Assuming an initial

white liquor and chip temperature of 170°F., the water from such wood/TADP = 2532 lb. ≡ 41.6 cu. ft. since the density of water is 60.8 lb./cu. ft. at this temperature. It is further assumed that the "basic density" of the wood (lb. o.d. wood/cu. ft. wet wood) is (0.40)(62.4) = 24.96 lb./cu.ft.

Restraint R3

In the cooking operation, it is assumed that black liquor acts simply as an inert diluent when mixed with white liquor so long as

$$\frac{V_{BL}}{V_{WL}} \leq K_3 .$$

Here, V_{BL} is the volume of recirculated black liquor, cu. ft./TADP, V_{WL} is the cu. ft. of white liquor/TADP, and K_3 is a limitation on the ratio of black to white liquor (see R3 of model) arising out of management policy and technical observation. If this ratio is $0.57 \leq K_3$ in the base case under consideration, V_{BL} = 83.3, since V_{WL} = 124.3. The total liquor volume (including chip moisture) = $V_L = V_{WL} + V_{BL} + 41.6$. In the base case, this is 249.2 cu. ft.

Concentration and Chemical-to-Wood Ratio

Let c_i equal initial concentration of active alkali:

$$c_i = \frac{(X1 + X2)(0.995)}{V_L} . \qquad (26)$$

The 0.995 reflects the ~0.5% loss of white liquor in the causticizing

operation. For the base case,

$$c_i = \frac{666.6}{249.2} = 2.675 \text{ lb./cu. ft.}$$

Let c_w = initial chemical-to-wood ratio:

$$c_w = \frac{(X1 + X_2)(0.995)}{3798} . \qquad (27)$$

For the base case,

$$c_w = \frac{666.6}{3798} = 0.1755 \text{ lb./lb.}$$

Restraints R4 and R8

Next, certain additional restrictions must be mentioned. The total volume of the solid wood substance plus V_L cannot exceed V_D. This represents a necessary equipment limitation. Also, suppose management has specified the liquor-to-wood ratio, V_L/w, to be at least K_4'. This limitation assures adequate chip coverage and circulation.

Letting Q = TADP/cook, these restraints can be expressed together:

$$\frac{V_D}{Q_w} - \frac{1}{(24.96)} + \frac{41.6}{w} \geq \frac{V_L}{w} \geq K_4' . \qquad (64)$$

or

$$\frac{V_D}{Q_w} - \frac{1}{24.96} + \frac{41.6}{w} \geq \frac{c_w}{c_i} \geq K_4' . \qquad (65)$$

The use of the volume of moisture in the wood (41.6) in conjunction with the basic density based on green wood volume underestimates the true magnitude of the left-hand side of Expressions (64) and (65). Penetration of liquor occurs during digester filling, but the amount cannot be accurately estimated. Interpretation of the optimum solution should bear this in mind. Thus, if a greater $\underline{V}_L$ (perhaps achieved by increasing $\underline{V}_{BL}$) than is allowed by the above limitation is desired, there is a certain amount of additional leeway to permit it. That is, if the restraint, R8, corresponding to the left-hand side of Expression (64) or (65) is critical, it can be relaxed some to allow for an improved effectiveness.

Incorporation of the Rate Expression

The values of $\underline{Q}$, $\underline{c}_i$, and $\underline{c}_w$ in Expression (65) are related to the kinetics of the cooking operation. The experimentally developed rate expression (see Appendices I and II) is:

$$\underline{t}_t = \frac{\ln \dfrac{[(\underline{K}\text{ no.})(0.292) - 2.53]\dfrac{\underline{Y}}{100} - 1.00}{25.00}}{(-5.22 \times 10^{-5})\left(\underline{e}^{40.00 - (16{,}100/\underline{T}_m)}\right)\left(\underline{c}_i - (0.0663)\dfrac{\underline{c}_i}{\underline{c}_w} - 5.05\right)}$$

$$\underline{t}_u\left[1 - \frac{(\underline{T}_m)^2}{16{,}100(\underline{T}_m - \underline{T}_o)}\right] \qquad (2)$$

where

$\underline{t}_t$ = total time of cook, min.,

$\underline{t_u}$ = time-up-to-temperature in a straight-line temperature rise period, min.,

$\underline{T_m}$ = maximum temperature, $^{\circ}$ abs.,

$\underline{T_o}$ = initial digester temperature, $^{\circ}$ abs.,

$\underline{c_i}$ = initial concentration of active alkali, g. (as Na_2O) /l.,

$\underline{c_w}$ = initial active alkali-to-wood ratio, g. (as Na_2O)/g.,

$\underline{K}$ no. = permanganate number, and

$\underline{Y}$ = pulp yield, %.

It is assumed for the purpose of this thesis that the rate expression for the cooking operation in the hypothetical kraft pulping system is Equation (2) with a 5%-decreased apparent rate constant. In addition, it is assumed that average initial digester temperature ($\equiv \underline{T_o}$) is always 150°F., maximum temperature ($\equiv \underline{T_m}$) is a constant 338°F. (170°C.), that the time-temperature schedule is straight line, and that sulfidity is a nondetermining variable provided it is $\geq$ 28% (see restraint R2). The resulting counterpart rate expression (making appropriate changes in constants to account for the difference in units used in this appendix) is:

$$\underline{t_t} = \frac{\underline{k_2}}{\underline{c_i} - \underline{k_3}\,\dfrac{\underline{c_i}}{\underline{c_w}} - \underline{k_4}} + \underline{k_5'}\,\underline{t_u} \qquad (66)$$

where

$\underline{k_2}$ = 96.82,

$\underline{k_3}$ = 0.0663,

$\underline{k_4}$ = 0.3153,

$\underline{k_5}' = 0.8885,$

and

$\underline{t_t}$ = total time of a cook, min.,

$\underline{c_i}$ = lb. active alkali (as Na_2O)/cu. ft.,

$\underline{c_w}$ = lb. active alkali (as Na_2O)/lb., and

$\underline{t_u}$ = time-up-to-temperature, min.

The importance of Equation (66) is in relation to the time necessary for a cook; and thus the wood charge per cook to give the required daily production; and therefore the allowable $\underline{V_L}$, which decreases as the wood charge per cook increases. Letting

$\underline{t_b}$ = min. between cooks,

and recalling that:

$\underline{R}$ = daily TADP required,

$\underline{n}$ = number of digesters,

1440 = min./day,

$\underline{t_t}$ = total time of a cook, min., and

$\underline{Q}$ = TADP/cook,

then

$$\underline{R} = \underline{nQ}[1440/(\underline{t_t} + \underline{t_b})], \text{ or}$$

$$\underline{Q} = \frac{\underline{R}(\underline{t_t} + \underline{t_b})}{\underline{n}(1440)} . \qquad (67)$$

In this thesis, $\underline{R}$ is fixed at 250 TADP/day, so that Equation (67) becomes

$$\underline{Q} = \frac{0.1736(\underline{t_t} + \underline{t_b})}{\underline{n}} . \qquad (68)$$

Substituting this expression for $\underline{Q}$ in the digester limitation expression [(65)], and multiplying through by $\underline{w}$ (= 3798), gives:

$$\frac{\underline{n}(15,553)}{\underline{t_t} + \underline{t_b}} - 110.6 \geq \underline{V_L} \geq \underline{K_4'w} = \underline{K_4} . \qquad (69)$$

The left-hand inequality of Expression (69) corresponds to R8; the right-hand inequality corresponds to R4.

Restraint R5

An additional realistic restraint (an operating limitation) will be imposed:

$$\underline{t_b} \geq \underline{K_5} \qquad (70)$$

where $\underline{K_5}$ is the minimum time necessary to discharge a digester and ready it for the next cook. This restraint corresponds to R5.

Feasibility of the Base Case With Respect to R4, R5, and R8

Assuming for the base case balance of this appendix that $\underline{t_u}$ = 90 min., Equation (66) gives $\underline{t_t}$ = 151.7 min.

Now, for the base case, let

$\underline{t_b}$ = 30 min.,

$\underline{n}$ = 5,

$\underline{K_4}$ = 213.1 (corresponding to a minimum liquor-to-wood ratio of 3.5 ml./g.), and

$\underline{K_5}$ = 30.

Then Expression (69) becomes

$$317.4 \geq 249.2 \geq 213.1$$

while Expression (70) becomes

$$30 \geq 30.$$

Thus, the various digester requirements (restraints R4, R5, and R8) are met in the base case.

Elimination of t_u From the Rate Expression

Equation (66) can be expressed in a more general form. The time-up-to-temperature, t_u, can be written as a function of V_L (the total volume of liquor circulated per TADP) and Q (TADP/charge). It is assumed that the following relationship always holds:

$$t_u = \beta V_L Q = \beta V_L \frac{(t_t + t_b)}{n} \frac{R}{1440} \qquad (71)$$

where β can be determined from a known situation. However, in originally developing this portion of the model, t_u was inadvertently expressed as a function of V_L only. As a result, Equation (66) became

$$t_t = \frac{k_2}{c_i - k_3 \frac{c_i}{c_w} - k_4} + k_5 V_L \qquad (25)$$

where $k_5 = 0.321$ (determined from base case conditions). Any effects resulting from the use of Equation (25), instead of the more accurate form [Equation (71) substituted into Equation (66)] are probably small,

and in any case of no importance in the framework of this thesis.

Specific Heats and Specific Gravities of Black and White Liquors

To complete the digester operation material balance, expressions for the specific heat and specific gravity of both the black liquor and the white liquor are needed.

The specific gravity of black liquor (sp. $gr._{BL}$) can be considered = $1.00 + 0.61\underline{s}$ where $\underline{s}$ is the weight fraction solids in the black liquor (40). The effect of organic/inorganic ratio is negligible.

The specific heat of black liquor (sp. $ht._{BL}$) can be calculated from an enthalpy-concentration diagram for a typical black liquor (40). The very slight effect of temperature on specific heat (41) is neglected. The resulting equation is sp. $ht._{BL} = 1 - 0.68\underline{s}$. Note that when $\underline{s} = 1.0$ (solid black liquor), the sp. $ht._{BL} = 0.32$, similar to 0.33, the specific heat of most woods and pulps.

Since the sp. $ht._{BL}$ when used in the balance of this thesis is always multiplied by the sp. $gr._{BL}$, this product is of interest. It is 0.96 ($\sim$1% error) for values of $\underline{s}$ between 0.18 and 0.25, the expected range in the optimizations.

The International Critical Tables show that Na_2S, Na_2SO_4, NaOH, and Na_2CO_3 each alone in solution have specific gravities easily calculable from a knowledge of the weight of salt dissolved per unit volume of solution. This is a result of there being only negligible volume change upon dilution. Thus, one would predict that white liquor specific gravity (sp. $gr._{WL}$) can also be directly calculated. This was

readily verified experimentally with white liquors having a wide range of compositions. The calculation is:

$$\text{sp. gr.}_{WL} = \frac{(0.995)\Sigma \underline{X}_a + 60.8\underline{V}_{WL}}{60.8\underline{V}_{WL}} \quad (\text{at } 170^{\circ}\text{F.})$$

In the base material balance, $\text{sp. gr.}_{WL} = 1.13$.

The specific heat of white liquor (sp. ht._{WL}) has been approximated by assuming that the entire inorganic composition of white liquor is NaOH, and thus the classical enthalpy-concentration diagram for NaOH can be employed [see reference (42)]. Using this and considering the temperatures and concentrations of ordinary white liquors,

$$\text{sp. ht.}_{WL} = 0.98 - 0.40 \frac{(0.995)\Sigma \underline{X}(80/62)}{(0.995)\Sigma \underline{X}(\frac{80}{62}) + 60.8\underline{V}_{WL}} .$$

In the base case, $\text{sp. ht.}_{WL} = 0.935$. As with sp. ht._{BL}, the sp. ht._{WL} is not used alone in any of the balances. Since it is always multiplied by the sp. gr._{WL}, the product of these two is of interest. It can be shown that over a wide range including typical concentrations, this product $\cong 1.06$ with only a $\sim 1\%$ error.

Water Lost During Relief and Blowing

Continuing with the material balance, assume that during any cook, 175 lb. of water vapor/TADP are lost in the digester relief vapors (39). At the end of the cook when the digester contents are blown into the blowtank, additional water is lost by flashing. To calculate this, Baker's method (39) is used. (In this thesis, each digester is assumed

to weigh 50,000 lb. and has an average heat capacity of 0.127.) The calculation follows:

$$\text{lb. water lost during blow/TADP} = \left(\frac{\underline{H}_1 - \underline{H}_2}{\underline{H}_3}\right)(\underline{I})$$

where

$$\frac{\underline{H}_1 - \underline{H}_2}{\underline{H}_3} = \frac{309.04 - 180.07}{1150.4} = 0.1121$$

where

$\underline{H}_1$ = enthalpy of saturated liquid water at 338°F.,

$\underline{H}_2$ = enthalpy of saturated liquid water at 1 atm.,

$\underline{H}_3$ = enthalpy of saturated water vapor at 1 atm., and

$\underline{I}$ = "water equivalent" of digester and contents

$$= 0.33\underline{w} + 0.67 + (60.8)(\text{sp. gr.}_{WL})(\text{sp. ht.}_{WL})\underline{V}_{WL} + (60.8)(\text{sp. gr.}_{BL})(\text{sp. ht.}_{BL})\underline{V}_{BL} + \frac{(0.127)(50,000)}{\underline{Q}} - 175$$

$$= \underline{w} + (60.8)(1.06)\underline{V}_{WL} + (60.8)(0.96)\underline{V}_{BL} + \frac{\underline{n}(6350)}{0.1736(\underline{t}_t + \underline{t}_b)} - 175.$$

Thus,

$$\underline{I} = 3623 + 64.4\underline{V}_{WL} + 58.4\underline{V}_{WL} + \frac{\underline{n}(36,578)}{\underline{t}_t + \underline{t}_b}. \qquad (13)$$

In the base material balance under consideration,

$$\underline{I} = 17,499.$$

Thus, lb. H_2O lost during blowing/TADP for the base case = (0.1121)(17,499) = 1962. (The value, $\underline{I}$, will be used later for determining the weight

fraction of solids in black liquor to the evaporators, and the digester steam requirements.)

Amount of Black Liquor and Pulp to Washers

Finally, it will be useful to calculate total lb. black liquor and pulp to the washers/TADP:

$$(60.8)(\text{sp. gr.}_{BL})\underline{V}_{BL} + (60.8)(\text{sp. gr.}_{WL})\underline{V}_{WL} + \frac{\underline{W}}{0.6} - 175 - (0.1121)(\underline{I})$$

$$= (60.8)(1 + 0.61\underline{s})\underline{V}_{BL} + (0.995)\Sigma\underline{X}_{\underline{a}} + (60.8)\underline{V}_{WL} + \frac{3798}{0.6}$$

$$- 175 - (0.1121)(\underline{I}).$$

In the base material balance, lb. black liquor plus pulp to washers/TADP = 17,815 + 3090$\underline{s}$. The value of $\underline{s}$ is determined later in this appendix.

WASHER OPERATION

The dilution curve is the most useful concept in describing the performance characteristics of washers (34, 43, 44, 45). It is a plot of loss of sodium (expressed as Na_2SO_4) per TADP, $\underline{L}_N$, vs. pounds of wash water (going from the washers and diluting the separated black liquor) per lb. of air-dried pulp, $\underline{D}$.

The dilution curve for the hypothetical multistage washer installed in the system under consideration is shown in Fig. 9. Its equation is:

$$\underline{L}_N = \frac{12.5}{\underline{D} + 0.085} + 12.0. \qquad (72)$$

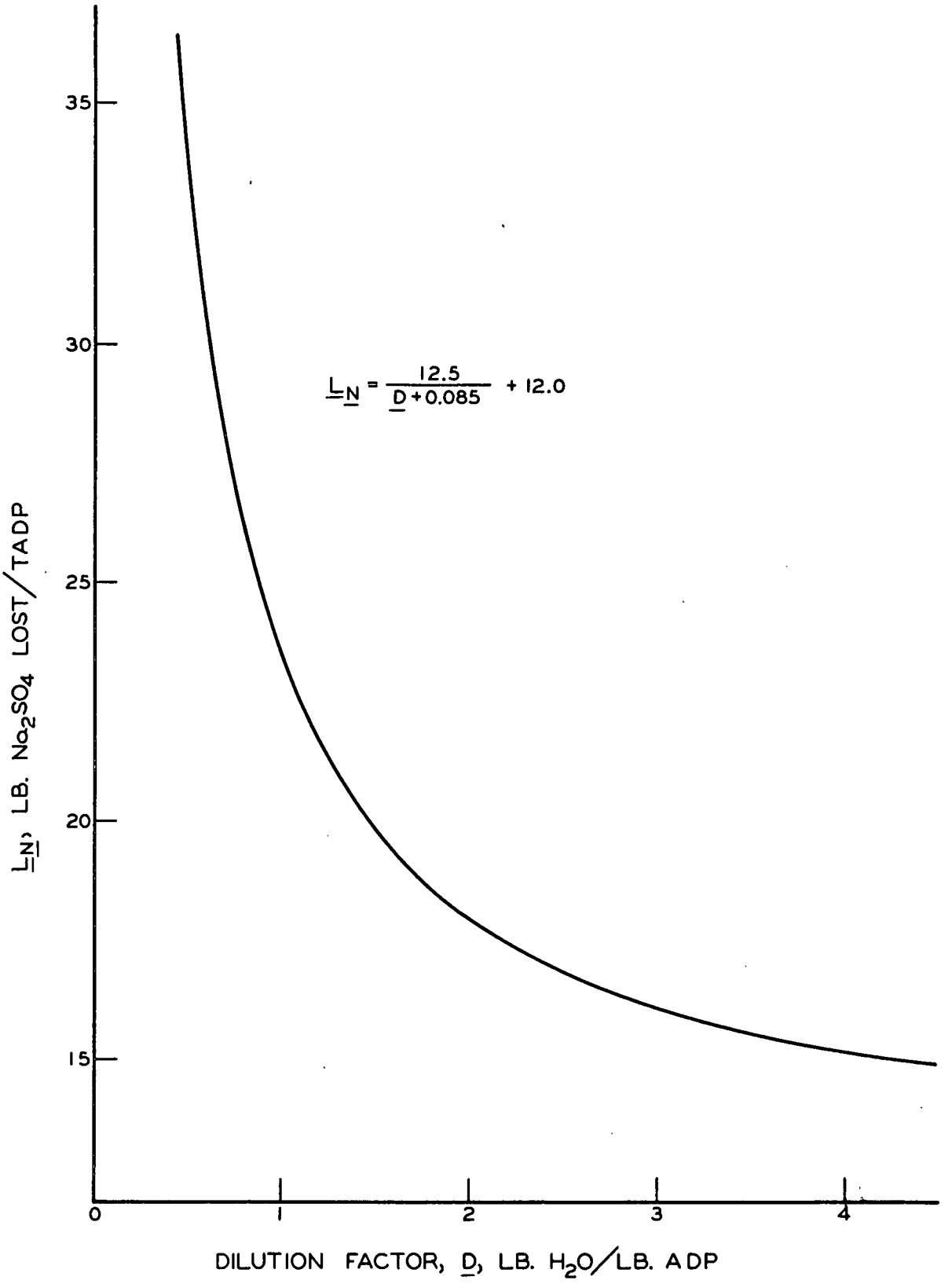

Figure 9. Dilution Curve for Multistage Washer in Hypothetical Pulping System

The dilution curve is always exponential in shape, as shown. The particular shape of a dilution curve depends on many factors including the type of equipment (number and size of drums, number of stages, etc.), how it operates (e.g., speed, wash water temperature, vacuum), and the kind and hardness (degree of cooking) of the pulp. For installed washer equipment operated in a fixed manner (as is considered in this thesis), the hardness and kind of pulp control the shape of the dilution curve. The curve given in Figure 9 is for an unbleached grade of spruce kraft market pulp ($\underline{K}$ no. = 25.0) and, say, a three-drum, four-stage washer.

The degree of washing depends on an economic balance of the factors involved in conjunction with consideration for the rest of the system. The less wash water used, the less evaporation necessary. But increases in inorganic chemical losses, and loss of potential high-pressure steam due to organic chemical losses, result. Also, there would be an increase in defoamer requirements in the screen room, proportional to the organic losses. The accompanying increased difficulty in deckering is not considered quantitatively here, since it is quite intangible. And increased alum consumption in the papermaking process (due to the presence of increased amounts of contaminating BL in the pulp) is not considered because the hypothetical pulp mill is not integrated. This could have, though, an important effect on customer relations. To illustrate this, a restraint, $\underline{R6}$, (limiting the amount of black liquor contamination in the washed pulp) has been built into the generalized mathematical model and will be discussed in Appendix IV. Wash water at $\underline{G}$ g.p.m. is used. More than enough heat to heat this wash water is assumed available from the blow steam heat recovery operation. The pulp consistency, $\underline{C_p}$, off the last drum is assumed in this thesis to

always be 16%.

An expression relating $\underline{D}$, $\underline{L_N}$, $\underline{C_p}$, and $\underline{G}$ when the daily production over the washers is 250 TADP is

$$\underline{D} = \frac{12{,}000\,\frac{\underline{G}}{250} - [1800(\frac{100}{\underline{C_p}} - 1.00) - (1.75)\underline{L_N}]}{2000}, \qquad (73)$$

where the 1.75 is the conversion factor from Na_2SO_4 equivalent to equivalent BLS for the system (34).

Now, let $\underline{\ell}$ = lb. BLS to evaporators (and furnace):

$$\underline{\ell} = 0.526\underline{w} + (0.995)\Sigma\underline{X_a} - (1.75)\underline{L_N}.$$

(Small amounts of sulfur gas losses are neglected.) In the base material balance, $\underline{\ell} = 2998 - (1.75)\underline{L_N} = 2970$. Thus,

$$\underline{L_N} = 16.0 \text{ lb. (as } Na_2SO_4).$$

In general,

$$\begin{aligned} \underline{s} &= \text{weight fraction solids} \\ &= \frac{\text{lb. BLS to evaporators}}{\text{total lb. black liquor to evaporators}} \\ &= \underline{\ell}/[(0.995)\Sigma\underline{X_a} + (60.8)\underline{V_{WL}} + (3798/0.6) - 175 - \\ &\quad (0.1121)\underline{I} - 1800 + 2000\underline{D} - (1.75)\underline{L_N}]. \qquad (74) \end{aligned}$$

Employing Equation (73), Equation (74) becomes:

$$\underline{s} = \underline{\ell}/[(0.995)\Sigma\underline{X_a} + (60.8)\underline{V_{WL}} + (3798/0.6) - 175 - (0.1121)\underline{I} - 1800 + 48\underline{G} - 1800(\frac{100}{\underline{C_p}} - 1.00)]. \qquad (75)$$

[Equation (75) becomes Equation (15) of the model for $\underline{C_p} = 16.$] For the base material balance being considered,

$$\underline{s} = \frac{2970}{1500 + 48\underline{G}}. \tag{76}$$

Now Equation (72) can be approximated by substituting an approximate value of $\underline{D}$, based on a typical loss, $\underline{L_N}$, of, say, 21 lb. Na_2SO_4 per TADP:

$$\underline{D} \cong \frac{6\,\underline{G}}{250} - 0.9\left(\frac{100}{\underline{C_p}} - 1.00\right) + 0.018 = 0.024\underline{G} - 4.71,$$

since $\underline{C_p} = 16.$ Using this approximate value of $\underline{D}$, Equation (72) becomes Equation (77):

$$\underline{L_N} \cong \frac{12.5}{(0.024\underline{G} - 4.71) + 0.085} + 12.0$$

$$= \frac{12.5}{(0.024)\underline{G} - 4.62} + 12.0. \tag{77}$$

Equation (77) is expressed more generally in the model as:

$$\underline{L_N} = \frac{\underline{k_6}}{(0.024)\underline{G} - \underline{k_7}} + \underline{k_8}. \tag{18}$$

Here, constants $\underline{k_6}$, $\underline{k_7}$, and $\underline{k_8}$ are related to the performance characteristics of the washer system.

Substituting the base case value of $\underline{L_N}$ (16.0) into Equation (72) gives $\underline{D} = 3.04$, and into Equation (77), it gives $\underline{G} = 323.0$. Substituting this value of $\underline{G}$ into Equation (76) gives $\underline{s} = 0.1747$ for the base material balance.

EVAPORATOR OPERATION

The evaporators considered are conventional, modern, sextuple-effect evaporators utilizing internal heaters. They are equipped with two-stage-liquor flash and live-steam-condensate flash systems, and a barometric condenser. Only the first effect is equipped with stainless steel tubes and all tube sheets are drilled to allow for future mill expansion. The tubes are considered to be clean.

The evaporator system is characterized by the performance data of Table IX which was kindly supplied at the author's request by Mr. W. G. Dedert of the Swenson Evaporator Co.

TABLE IX
EVAPORATOR PERFORMANCE DATA

		ℓ		
		2800	3100	3400
s				
0.15	S.E.	5.00	5.00	5.00
	C_e	$184,950	$194,250	$203,750
0.20	S.E.	4.80	4.80	4.80
	C_e	$158,500	$166,600	$174,000
0.25	S.E.	4.64	4.64	4.64
	C_e	$134,050	$142,400	$149,500

The steam supplied is that indicated in Table X which is discussed in the next section. In all cases, the evaporation has been to 52% solids out of the evaporators, regardless of s, weight fraction solids in the weak black liquor. More or less evaporation, depending on s and the load, ℓ, requires a larger or smaller evaporative surface and thus a higher or lower installed cost. This is a design feature. In

conjunction with this, a limitation to the capital available for the purchase of evaporators, $\underline{K}_7$, is expressed in the model by restraint $\underline{R}7$. For equipment installed, the evaporator surface is fixed and the effect of outgoing black liquor characteristics on steam economy (S.E.), evaporator capacity, furnace operation, etc., must also be determined in construction of an appropriate model.

Figure 10 shows relationships, based on the data of Table IX, relating installed evaporator cost ($\underline{C}_e$) and S.E. to $\underline{s}$ and $\underline{\ell}$. Equations relating these variables are:

$$\underline{C}_e = 148{,}000 - (331{,}000)\underline{s} + (40)\underline{\ell} - (61)\underline{s}\underline{\ell}, \text{ and} \qquad (16)$$

$$\underline{S.E.} = 5.52 - (3.60)\underline{s}.$$

Steam economy is independent of $\underline{\ell}$.

The water rate to the condenser and hence water cost, associated pumping costs, etc., are neglected here as are such costs elsewhere in this thesis. The effect is felt to be negligible.

In the base material balance:

$\underline{C}_e$ = \$177,324, and

$\underline{S.E.}$ = 4.89.

It is assumed that $\underline{K}_7$ of $\underline{R}7$ is $\geq$ \$177,324.

lb. water evaporated = $(\underline{\ell}/\underline{s})(1 - \underline{s}/0.52)$.

(In the base case, lb. water evaporated = 11,289.) The pounds of water evaporated, in conjunction with the S.E., determines the evaporator steam consumption in the energy balance.

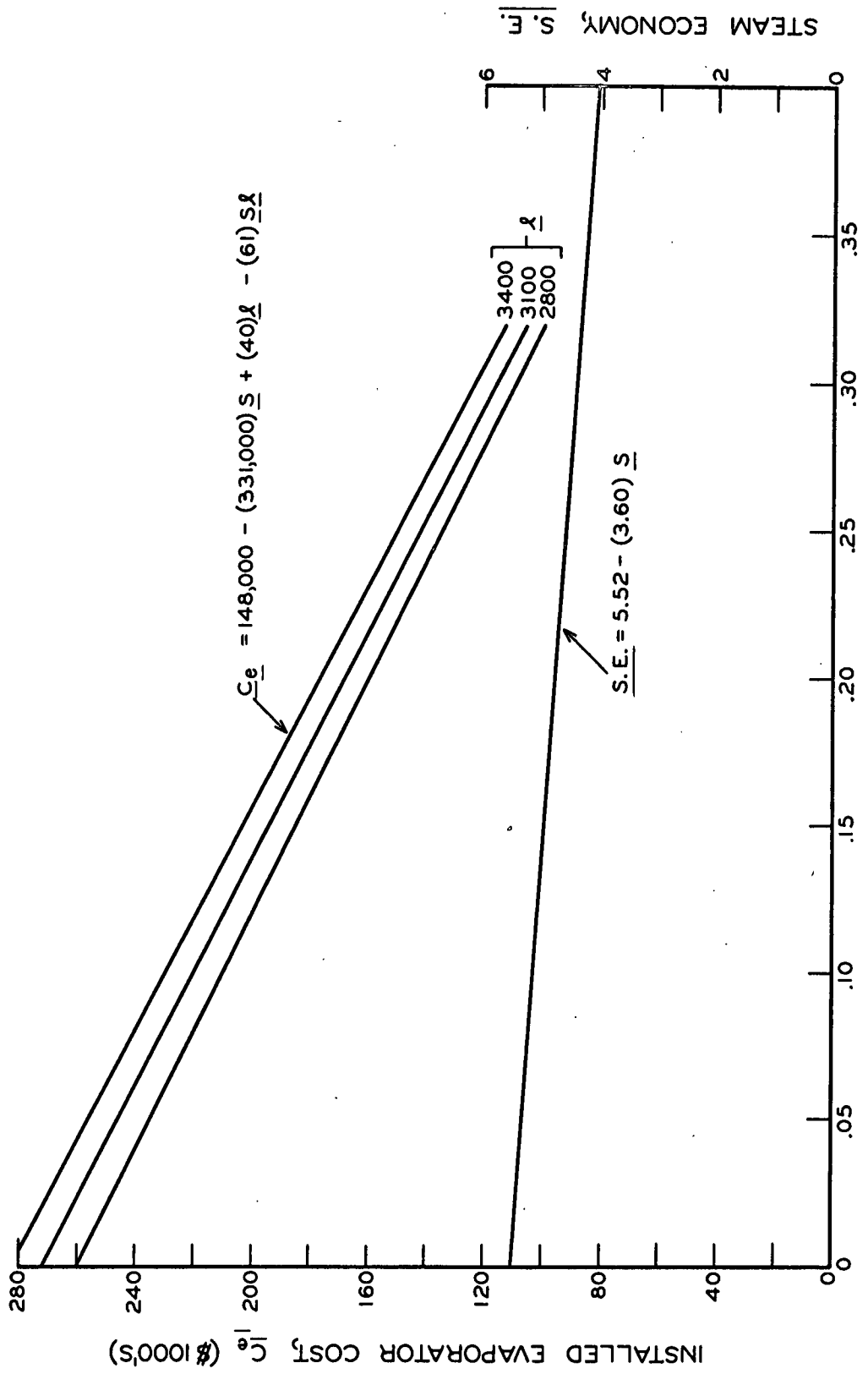

Figure 10. Relationships Between $\underline{C_e}$, $\underline{S.E.}$, $\underline{s}$, and $\underline{\ell}$ for Hypothetical Pulping System Evaporators

THE BASE ENERGY BALANCE[a]

The object of the energy balance is to compute gross high-pressure steam generated in the boiler and to determine the steam requirements for cooking, black liquor heating, and evaporation. This will then allow for a calculation of the amount (and dollar value) of the electricity and extra low-pressure steam generated. (The relatively small and constant requirements for steam for recovery unit blowdowns, and electricity for auxiliary operation, etc. are neglected.)

Table X gives the steam conditions at the boiler, turbine, digesters, and evaporators (34, 39, 46-48). Suppose the system is equipped with a double extraction noncondensing turbine. Steam is generated in the recovery boiler at 450 p.s.i.a. and 700°F. Such steam is superheated by 243.7° and has an enthalpy ("heat content") of 1359.9 B.t.u./lb. Its entropy is 1.6250 B.t.u./°F. All of this steam expands through the first part of the turbine and generates electricity by driving the turbogenerator. Each pound of steam here will generate 70.86/3413 kw.-hr. electricity if a 60% over-all efficiency is assumed. Thus, 0.60(1359.9 - 1241.8) = 70.86 B.t.u./lb., and there are 3413 B.t.u./kw.-hr.

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[a] Basis: 1 TADP unless otherwise stated.

TABLE X
STEAM CONDITIONS

Basis: 1 lb. Steam; Feedwater Temp. = 220°F., $\underline{H}_L$ = 188.1

		p.s.i.a.	°F.	°Supht.	Enthalpy of Supht'd Vapor $\underline{H}_V$	Enthalpy of Sat'd Liquid $\underline{H}_L$	Latent Heat of Vap'n + Supht. $\underline{H}_{VL}$	Entropy of Supht'd Vapor $\underline{S}_V$
Boiler and Turbine Throttle		450.0	700.0	243.7	1359.9			1.6250
	kw.-hr./lb. = $\frac{70.86}{3413}$ at 60% eff.							
First-Stage Extraction	ideal (isentropic)	150.0	439.7	81.3	1241.8			1.6250
	actual (RCR = .70)	150.0	505.9	147.5	1277.2			1.6631
BL Heater / Digesters	Point of Use	150.0	480.9	122.5	1264.1	330.5	933.6	
	kw.-hr./lb. = $\frac{55.20}{3413}$ at 60% eff.							
Second-Stage Extraction	ideal (isentropic)	55.0	304.2	17.1	1185.2			1.6631
	actual (RCR = .70)	55.0	357.1	70.0	1212.8			
Evaporators / Surplus	Point of Use	55.0	332.1	45.0	1199.9			

The first-stage extraction provides process steam at 150 p.s.i.a. for use in black liquor heating and cooking. An ideal (isentropic) expansion of steam to this condition never occurs, and with a Rankine Cycle Ratio (R.C.R.) of 0.70, the enthalpy drop is 0.70 times the ideal drop, or 0.70(1359.9 - 1241.8), and thus the enthalpy after expansion is 1277.2 B.t.u./lb. The condition of such steam can be determined from steam tables. During transfer of the steam to point of use (e.g., digesters), it is assumed to lose 25° of superheat. The heat given up at the digesters is 933.6 B.t.u. per pound of steam condensed since it is assumed that the condensate is not cooled there.

Only part of the steam entering the turbine is required by the black liquor heaters and the digesters. The remainder expands further in the second part of the turbine, and generates more electricity at 60% efficiency until its pressure is 55 p.s.i.a., when it leaves the turbine. Again, in the distribution of this low-pressure steam (primarily to the evaporators), 25° superheat are assumed lost.

It is felt that profitable operation of the system will always provide a positive surplus of low-pressure steam. Thus, such a requirement will not be specified explicitly as a restraint in the optimization.

The clean condensate from the digester and evaporator operations is returned to the "hot well" where sufficient make-up water is added for the generation and distribution of steam in the next cycle.

The feedwater temperature is assumed to be $220^{\circ}F$. The enthalpy of saturated liquid water at this temperature is 188.1 B.t.u./lb.

Some additional information concerning the recovery furnace is necessary for developing the energy balances:

1. Laboratory heating value of 1 lb. BLS characterizing the system on which the base calculations are being made = 6710 B.t.u.
2. Temperature of black liquor to direct-contact evaporators = 200°F.
3. Temperature of black liquor from direct-contact evaporators = 190°F.
4. Temperature of black liquor fired to furnace = 240°F.
5. Temperature of flue gases leaving unit = 300°F.
6. Temperature of smelt = 1550°F.
7. Recovery room air at 80°F., 60% R.H., 30 in. Hg
8. Sp. ht. of BLS = 0.32
9. Sp. ht. of smelt = 0.32
10. Sp. ht. of water vapor = 0.45
11. Sp. ht. of dry flue gases = 0.24
12. Excess air = 23%
13. Heat of Na_2SO_4 reduction (including C loss) = 3000 B.t.u./lb.
14. Heat of fusion of smelt = 61 B.t.u./lb.
15. Radiation and unaccounted-for losses are assumed 4% total heat input.

The energy balance over the recovery furnace, up to the calculation of gross high-pressure steam generated, follows the method of Tomlinson and Swartz (34). Here, the first step is to calculate the composition of the flue gas from the recovery unit (see last line, Table XI). To do this, the following preliminary calculations are necessary:[a]

[a] Basis: 1 lb. BLS, 80°F.

TABLE XI

CALCULATION OF AIR REQUIREMENTS AND PRODUCTS OF COMBUSTION IN BURNING 1 LB. BLS*

Calculation Step		Theoretical Oxidant Req'd O_2	Theoretical Oxidant Req'd Air	Products of Combustion CO_2	Products of Combustion SO_2	Products of Combustion O_2	Products of Combustion N_2	Water from BLS	Water from Air	Total
Amounts of flue gases from 1 lb. BLS	C = 0.3847	1.0259	4.4934	1.4106			3.4162		0.0585	0.0585
	H_2 = 0.0407	0.3256	1.4261				1.0842	0.3663	0.0186	0.3849
	S = 0.0024	0.0024	0.0105		0.0048		0.0080		0.0001	0.0001
	O_2 = 0.1017					0.1017				
	N_2 = 0.0018						0.0018			
	Total	1.3539	5.9300	1.4106	0.0048	0.1017	4.5102	0.3663	0.0772	0.4435
Add O_2 released during reduction						0.0745				
	Total	1.3539	5.9300	1.4106	0.0048	0.1762	4.5102	0.3663	0.0772	0.4435
Subtract air and air component equivalents of O_2 from BLS + O_2 from reduction (0.1017 + 0.0745 = 0.1762)		0.1762	0.7718			0.1762	0.5867		0.0100	0.0100
	Difference	1.1777	5.1582=theoretical air req'd.	1.4106	0.0048	0.0000	3.9235	0.3663	0.0672	0.4335
Add x's air (assumed 23%)		0.2709	1.1864			0.2709	0.9021		0.0154	0.0154
	Total	1.4486	6.3446	1.4106	0.0048	0.2709	4.8256	0.3663	0.0826	0.4489
Add H_2O in strong BL (= .48/.52 = 0.9231) and condensate from steam liquor heater (= .0406). Total = 0.9637.								0.9637		0.9637
	Total	1.4486	6.3446	1.4106	0.0048	0.2709	4.8256	1.3300	0.0826	1.4126
				dry flue gas = 6.5119						

* Fraction solids in strong BL = .52; air: 80°F., 30 in. Hg, 60% R.H.; 1 lb. O_2 ≡ 4.38 lb. humid air ≡ 3.33 lb. N_2 ≡ 0.057 lb. moisture.

1. Lb. water evaporated in direct-contact evaporators:

	Fraction Solids	Solids	Total	H_2O
In	0.52	1.0	1.923	0.923
Out	0.65	1.0	1.538	0.538
			water evaporated =	0.538

It is assumed that a fraction solids of 0.65 out of the direct-contact evaporators is ideal (47).

2. Lb. steam used to heat black liquor =

$$\frac{[(0.32)(1.0) + (1.0)(0.538)](240 - 190)}{1264.1 - (240 - 32)} = 0.0406$$

3. Amounts of flue gases from 1 lb. BLS in base material and energy balances being calculated:

$$C = \frac{1142.5}{2970} = 0.3847$$

$$H_2 = \frac{120.9}{2970} = 0.0407$$

$$S = \frac{7.1}{2970} = 0.0024$$

$$O_2 = \frac{302.1}{2970} = 0.1017$$

$$N_2 = \frac{5.4}{2970} = 0.0018$$

4. O_2 released during reduction = 221.3/2970 = 0.0745

5. Lb. Na_2S (as Na_2O) formed by reduction = 214.4/2970 = 0.0722

6. Actual weight of smelt = 1195.9/2970 = 0.4027

GROSS HIGH-PRESSURE STEAM GENERATED

Table XII displays the actual heat balance over the recovery furnace, giving the heat ($\underline{H_b}$) in the high-pressure steam generated in the base case. With a feedwater temperature of 220°F., pounds of high-pressure steam generated per TADP in the base energy balance is

$$\left(\frac{\underline{H_b}}{1359.9 - 188.1}\right) = \frac{(4044.0)(2970)}{1171.8} = \frac{1.2011 \times 10^7}{1171.8} = 10{,}250.$$

STEAM REQUIREMENTS AT THE BLACK LIQUOR HEATERS, DIGESTERS, AND EVAPORATORS

To complete the energy balance (48), it is necessary to calculate the first-stage steam required by the digesters and the second-stage steam required by the evaporators. (The first-stage steam required by the black liquor heaters has already been calculated as 0.0406 lb./lb. BLS, or (0.0406)(2970) = 120.6 lb./TADP.)

The B.t.u./TADP required by the digesters (39) is:

$$(\underline{I} + 175)(338 - 150) + \frac{582(3.21\underline{t_t} - 1.51\underline{t_u})}{(0.1736/\underline{n})(\underline{t_t} + \underline{t_b})} + (175)(880.6)$$

$$= (188)\underline{I} + \underline{n}\,\frac{(1.076)(10^4)\underline{t_t} - (5.062)(10^3)\underline{t_u}}{(\underline{t_t} + \underline{t_b})} + (1.870)10^5,$$

where

880.6 = latent heat of saturated water vapor from relief at 338°F.,

TABLE XII
HEAT BALANCE OVER FURNACE (Base Case)
Basis: B.t.u./lb. BLS; 80°F.

Heat Input

1.	Heating value of BLS	= 6710.0
2.	Sensible heat in BL to unit [(0.32)(1.0) + (1.0)(0.923)](200 - 80)	= 149.2
3.	Sensible and latent heat in BL heating steam (0.0406)[1264.1 - (80 - 32)]	= 49.4
	Total heat input	= 6908.6

Heat Distribution

4.	Sensible heat of dry flue gas (6.5119)(0.24)(300 - 80)	= 343.8
5.	Sensible heat of moisture in flue gas (1.4126)(0.45)(300 - 80)	= 139.8
6.	Latent heat of moisture in flue gas (1.3300)(1048.6)	= 1394.6
7.	Heat required for reduction of Na_2SO_4 (0.0722)142/62 (3000)	= 496.1
8.	Heat of fusion of smelt (0.4027)61	= 24.6
9.	Sensible heat of smelt (0.4027)(0.32)(1550 - 80)	= 189.4
10.	Radiation and unaccounted-for losses (4% of total heat input)	= 276.3
11.	Heat in gross h.-p. steam gen. (by difference)	= 4044.0
		= $\underline{H_b}/2970$
	Total heat distributed	= 6908.6

$$\frac{0.1736}{\underline{n}}(\underline{t_t} + \underline{t_b}) = \underline{Q} = \text{TADP/cook, and}$$

$582(3.21\underline{t_t} - 1.51\underline{t_u})$ = radiation loss per cook calculated from the laws of radiation using data from a typical case (39) for equipment similar to this system's to fix the rate constant.

With little loss in accuracy, the radiation term will be fixed at its base case value in the general case. Then, the lb. 150 p.s.i.a. steam ($\underline{H_{VL}}$ = 933.6, see Table X) required by the digesters per TADP is:

$$(\frac{188}{933.6})\underline{I} + 235 = (0.2014)\underline{I} + 235.$$

In the base energy balance, this steam requirement is 3759 lb.

Finally, pounds of second-stage (55 p.s.i.a.) steam required by the evaporators equals

$$\frac{\text{water evaporated}}{\text{S.E.}} = \frac{\underline{\ell}/\underline{s}(1 - \underline{s}/0.52)}{5.52 - (3.60)\underline{s}}.$$

In the base energy balance, lb. steam required for evaporation/TADP = 11,289/4.89 = 2309.

REVENUES, COSTS, AND EFFECTIVENESS FOR THE BASE CASE

Now, with the material and energy balances established, the revenues and costs, and thus the effectiveness of the base case, can be determined. When this effectiveness is expressed in general terms as a function of the independent variables, it is then called the effectiveness function. The effectiveness function is developed, along with the rest of the model, in Appendix IV.

The following cost and revenue information is necessary for the calculations:

1. Let the capital recovery factor (crf) for the evaporators be based on an expected life of 15 years with no terminal salvage value, and a 10% interest rate. Therefore, (crf) = 0.13147 (49).

2. Cost of salt cake make-up = \$28.00/ton Na_2SO_4.

3. Cost of quicklime = \$23.00/ton CaO.

4. Cost of limekiln fuel = $k_9/10^6$ B.t.u. (In the base case, let k_9 = \$0.40.)

5. Cost of defoamer = \$0.0125/lb. of salt cake lost from washers per TADP when L_N = 16.0. (This is an approximate figure based on an actual operation.*)

6. Value of electricity generated = \$0.005/kw.-hr.

7. Value of surplus low-pressure steam = \$0.50/1000 lb.

It should also be noted that amortization of the evaporators in an existing mill is one of the many constant costs. However, in this thesis, for illustrative purposes, evaporator size (surface) and thus amortization has been left variable, and so is determined implicitly as a function of the optimum levels of the operating variables.

The measure of effectiveness, E, is the net return from the system. This is defined as revenues minus variable costs. The

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* This information was kindly supplied by P. H. West, Thilmany Pulp and Paper Company, Kaukauna, Wis.

effectiveness of the base case under consideration (E_b) is determined as follows:

Basis: 1 TADP

Revenues

1. Value of electricity generated (refer to Table X)

from 450-150 p.s.i.a.:

$$(10{,}250)\left(\frac{70.86}{3413}\right)(\$0.005) = \$1.064$$

from 150155 p.s.i.a.:

$$(10{,}250 - 3759 - 120.6)\left(\frac{55.20}{3413}\right)(\$0.005)$$

$$= (6370)\left(\frac{55.20}{3413}\right)(\$0.005) = 0.515$$

2. Value of surplus 55 p.s.i.a. steam:

$$(6370 - 2309)(\$0.0005) = (4061)(\$0.0005) = 2.030$$

Total revenues = \$3.609

Variable costs

1. Capital recovery plus interest on evaporator (assuming a 350-day year):

$$\frac{(0.13147)C_e}{(350)(250)} = (1.5025)(10^{-6})(\$177{,}324) = \$0.266$$

2. Cost of salt cake make-up:

$$(19.3)\left(\frac{142}{62}\right)\frac{\$28.00}{2000} = (19.3)(0.0321) = 0.620$$

3. Cost of lime make-up:

$$0.04\left(1.10\ \frac{56}{62}\ \frac{X1}{0.90}\right)\frac{\$23.00}{2000} = X1(0.000508)$$

$$= 455.5(0.000508) = 0.231$$

4. Fuel cost for lime kiln:

$$9 \times 10^6 \frac{0.96}{2000} (1.10 \frac{56}{62} \frac{\underline{X}1}{0.90}) \frac{\underline{k}_9}{10^6} = (0.00477)(\underline{k}_9)\underline{X}1$$

For $\underline{k}_9$ = \$0.40, fuel cost = 0.869

5. Cost of defoamer:

(\$0.0125)(16.0) = 0.200

Total variable costs = \$2.186

Thus, the net return = \$3.609 - \$2.186 = \$1.423. This is the effectiveness, $\underline{E}_b$, of the system when operating at the base conditions.

APPENDIX IV.

THE GENERALIZED SYSTEM - CONSTRUCTION OF THE MODEL

In order to determine the levels of the independent variables giving maximum effectiveness, a generalized mathematical model of the system must be developed and subjected to appropriate optimization techniques. The material and energy balances, and revenue and cost calculations of Appendix III facilitate the development of a generalized effectiveness function and the functional restraints applying to its optimization. The resulting generalized mathematical model is developed here and appears in the text of the thesis as Exhibit I.

THE GENERALIZED HEAT BALANCE

Exhibit III develops the generalized heat balance over the recovery furnace. This is a generalization of the base case heat balance in Table XII of Appendix III. Consideration of the base case results and their generalizations, neglect of the effect of small losses, and analysis of contributing sources in Table XI of Appendix III allow a simplified, yet accurate, generalized heat balance to be made.

AN EXPRESSION FOR L_o

It is necessary to have a generalized expression for organic matter lost at the washers/TADP, L_o. This is of importance in items 1 and 4 of Exhibit III because the heating value of the BLS and the amounts of flue gases from the BLS are directly proportional to the organic matter present. A general expression for L_o is also required for determining the generalized defoamer cost and restraint R6 which places a limit on the black liquor contamination tolerable in the washed

EXHIBIT III
GENERALIZED HEAT BALANCE OVER RECOVERY FURNACE
Basis: B.t.u./TADP

Heat Input

1. Heating value of BLS = $(6710)(2970)\frac{1998}{1979}\left(1 - \frac{1.75L_N}{(0.995)\Sigma X_a + 1998}\right)$

2. Sensible heat in BL to unit = $150[(0.995)\Sigma X_a + 1998 - 1.75L_N]$

3. Sensible and latent heat in BL heating steam = $50[(0.995)\Sigma X_a + 1998 - 1.75L_N]$

Heat Distribution

4. Sensible heat of dry flue gas = $(344)(2970)\frac{1998}{1979}\left(1 - \frac{1.75L_N}{(0.995)\Sigma X_a + 1998}\right)$

5. Sensible heat of moisture in flue gas = $140[(0.995)\Sigma X_a + 1998 - 1.75L_N]$

6. Latent heat of moisture in flue gas = $1395[(0.995)\Sigma X_a + 1998 - 1.75L_N]$

7. Heat required for reduction of Na_2SO_4 = $[(496)(2970) - .95(19.3 - M)\frac{142}{62}(3000)] \cong (496)(2970)$

8. Heat of fusion of smelt = $61\Sigma X_s$

9. Sensible heat of smelt = $470\Sigma X_s$

10. Radiation and unaccounted-for losses = $(276.3)(2970) = 820,611$ (assume constant)

11. Heat in gross high-pressure steam generated = H (by difference)

$$H = (1.413)(10^7) - (1328)\Sigma X_a - (531)\Sigma X_s + \frac{[(2324)\Sigma X_a - (2.874)(10^7)]L_N}{(0.995)\Sigma X_a + 1998} \qquad (12)$$

pulp. The generalized expression for $\underline{L}_o$ is

$$\underline{L}_o = (1.75)(\underline{L}_N) \frac{1998}{(0.995)\Sigma \underline{X}_a + 1998} . \qquad (78)$$

For item 1 of Exhibit III, the uncorrected heating value of the BLS for a general case is the heating value of the base case [(6710)(2970)] times the ratio of the general $\underline{L}_o$ [Equation (78)] to the base case $\underline{L}_o$. This ratio gives rise to the term:

$$\frac{1998}{1979} \left(1 - \frac{(1.75)\underline{L}_N}{(0.995)\Sigma \underline{X}_a + 1998}\right).$$

This same term also appears in item 4 of Exhibit III.

Defoamer Costs and Restraint R6

Defoamer cost for the base case is given in Appendix III as \$0.0125/lb. Na_2SO_4 lost or (\$0.0125/1.75) per lb. BLS lost. It is assumed that the requirement for defoamer is directly proportional to the organic matter lost, $\underline{L}_o$. Thus, in general, defoamer cost is

$$\frac{0.0125}{1.75} \frac{2998}{1998} \underline{L}_o .$$

The 2998/1998 is the base case ratio of BLS to organic matter.

Finally, restraint $\underline{R}6$ (a customer or market restraint) places a limit on $\underline{L}_o$:

$$\underline{L}_o \leq \underline{K}_6$$

or

$$\underline{R}6 = \underline{K}_6 - \underline{L}_o \geq 0. \qquad (79)$$

Equation (79) is essentially Equation (9) of the model.

ADDITIONAL CONSIDERATIONS

In item 5 of Exhibit III, the primary source of flue gas moisture is seen (from Table XI of Appendix III) to be the water in the black liquor from the evaporators. Since the evaporators feed a constant per cent solids to the furnace, this water is proportional to the BLS feed.

Where inconsequential, an average soda loss of 4.0 lb. (as Na_2O) from the causticizing operation is assumed.

In item 7 of Exhibit III, it is recognized that, except in the case of probably a minor amount of sulfur in the form of Na_2SO_4 present in the BLS to the furnace, the sulfur is in a reduced state and gives off heat during combustion. This liberated heat is compensated for by the endothermic reduction. Thus, only the amount of added salt cake--already oxidized--is considered in developing the generalized case here. However, since $\underline{M}$ will not vary too much from the base case value of 19.3, an average $\underline{M}$ of 19.3 is used, and item 7 becomes constant, with virtually no loss of accuracy.

The lb. gross high-pressure steam per TADP generated in the general case is $\underline{H}/1171.8$.

CONSTRUCTION OF THE MODEL

Exhibit IV displays the individual and total generalized system revenues and costs.

EXHIBIT IV
GENERALIZED SYSTEM REVENUES AND COSTS
Basis: $/TADP

Revenues

1. Value of electricity generated at 450 - 150 p.s.i.a. = $\frac{H}{1171.8} \frac{70.86}{3413} (0.005)$

2. Value of electricity generated at 150 - 55 p.s.i.a. = $\left\{\frac{H}{1171.8} - [(0.2014)I + 235] - (0.0406)\ell\right\} \cdot \frac{55.20}{3413} (0.005)$

3. Value of surplus 55 p.s.i.a. steam = $\left\{\frac{H}{1171.8} - [(0.2014)I + 235] - (0.0406)\ell - \frac{\ell/s(1 - s/0.52)}{5.52 - (3.60)s}\right\}(0.0005)$

Total revenues = $(5.843)(10^{-7})H - (1.170)(10^{-4})I - (2.358)(10^{-5})\ell - \frac{(\ell/s - \ell/0.52)(10^{-4})}{1.104 - (0.72)s} - (1.365)(10^{-1})$

Variable costs

4. Cost of capital recovery plus interest on evaporators = $1.502(10^{-6})C_e$
5. Cost of salt cake make-up = $(0.0321)M$
6. Cost of lime make-up = $(0.000508)X1$
7. Fuel cost for lime kiln = $(0.00477)(k_9)X1$
8. Defoamer cost = $\frac{(37.48)L_N}{(0.995)\Sigma X_a + 1998}$

Total variable costs = $1.502(10^{-6})C_e + (0.0321)M + (5.08)(10^{-4})X1 + (4.77)(10^{-3})(k_9)X1 + \frac{(37.48)L_N}{(0.995)\Sigma X_a + 1998}$

Exhibit I (in the body of the thesis) gives the mathematical model consisting of an effectiveness function ($\underline{e}$) to be maximized, eight restraint expressions, and a number of subsidiary equations. These latter are based on material balance equations generalized from Appendix III and determine nonindependent variables appearing in the effectiveness function and restraint expressions. There are 5 independent variables in the model. These can be chosen quite arbitrarily; the five used in this thesis are: $\Sigma\underline{X} = \underline{Y}1$, $\underline{V}_{WL} = \underline{Y}2$, $\underline{V}_{BL} = \underline{Y}3$, $\underline{G} = \underline{Y}4$, and $\underline{t}_b = \underline{Y}5$.

In developing the model, it is assumed in the expression for $\underline{M}$ that the fume and causticizing operation soda losses are always proportional to the organic load ($\Sigma\underline{X} = \underline{Y}1$).

Loss of inorganic matter from the washers, $\underline{L}_i$, is figured in the same way as $\underline{L}_o$:

$$\underline{L}_i \text{ (as } Na_2O) = \frac{(1.75)\underline{L}_N(0.995)\Sigma\underline{X}}{(0.995)\Sigma\underline{X}_a + 1998}.$$

The expression for $\underline{X}3$ in the model was determined as follows:

By a sulfur balance -

$$\underline{M}\frac{32}{62} \cong \frac{(8.3)\underline{Y}1}{752.3}\frac{32}{62} + \frac{4.0(\underline{X}2 + \underline{X}3)}{752.3}\frac{32}{62} + \frac{(1.75)\underline{L}_N(0.995)(\underline{X}2 + \underline{X}3)}{(1.33)\underline{Y}1 + 1998}\frac{32}{62}$$

$$+ \delta + (1 - \epsilon)\underline{Z}; \quad \delta'(1 - \epsilon) \geq 0, \tag{80}$$

where

$\underline{Z}$ = total load of sulfur to the furnace,

$(1 - \epsilon)$ = fraction of $\underline{Z}$ lost in flue gases, and

δ = sulfur gas lost from system at locations other

than the furnace. Assume all of this loss occurs around the evaporators. Assume effect on load, $\mathcal{L}$, is negligible.

$(1.33)\underline{Y1} \cong (0.995)\Sigma\underline{X}_a$, a simplifying approximation.

The value of δ can be approximated as

$$\delta \cong \frac{\delta'(\underline{X2} + \underline{X3})}{225.7} \tag{81}$$

where $\delta' \geq 0$ is a known value of δ when the base case $(\underline{X2} + \underline{X3}) = 225.7$.

Using the operating assumption that $(\epsilon\underline{Z})$ of the sulfur to the furnace is retained in the smelt as Na_2SO_4:

$$\underline{X2} + \underline{X3} = \epsilon\underline{Z}\frac{62}{32} + \underline{M} - 8.3\frac{\underline{Y1}}{752.3} . \tag{82}$$

Substituting Equation (81) into Equation (80) and solving for $\underline{Z}$; then substituting this expression for $\underline{Z}$ into Equation (82); and finally solving the resulting expression for $\underline{X3}$, using Equation (20) of the model, gives:

$$\underline{X3} = \left[\frac{(1.33)(0.05)(4.0)(\underline{Y1})^2}{752.3} + \frac{(1998)(0.05)(4.0)\underline{Y1}}{752.3} + (1.75)(0.05)\underline{L_N}(0.995)\underline{Y1}\right] + \left\{(1 - \epsilon)[(1.33)\underline{Y1} + 1998] + \frac{\epsilon(1.33)\underline{Y1}(4.0)}{752.3} + \frac{\epsilon(1998)(4.0)}{752.3} + \epsilon(1.75)\underline{L_N}(0.995) + \epsilon\frac{62}{32}\frac{\delta'(1.33)\underline{Y1}}{225.7} + \epsilon\frac{62}{32}\frac{\delta'(1998)}{225.7}\right\} . \tag{83}$$

For a given ϵ and δ', Equation (83) can be simplified somewhat.

In originally setting up X3 for the computer program, an oversight was made. The effect of this inadvertence is that in the mathematical model, $\epsilon = 1.0$ (corresponding to no loss of S gas from the furnace), and $\delta' = 3.5$ (rather than the impossible -3.6 for the base case of Appendix III, which assumed an $\epsilon = 0.96$). Employing an $\epsilon = 1.0$, the energy balance of Appendix III, and thus the generalized expressions in the model, are at most only negligibly affected in the framework of this thesis. Equation (21) of the model, then, is entirely suitable, and results from Equation (83) when $\epsilon = 1.0$ and $\delta' = 3.5$. The $(2.377)(10^{-3}) \cdot L_N(Y1)$ term in Equation (21) is approximately equal to the $\epsilon(1.75)L_N \cdot (0.995)$ term of Equation (83) for $Y1 = 752.3$ and $\epsilon = 1.0$.

APPENDIX V.

THE CREATED RESPONSE SURFACE TECHNIQUE

THE APPROACH

The object of any optimization is to find in some way the values of the independent variables which maximize the effectiveness of the system, subject to nonviolation of any restraints at the optimum. As indicated in the section of this thesis entitled "Optimization," the violation of restraints during an optimization may be only temporary and thus not crucial at the optimum. In general, though, it is risky to rely on this happening because the nature of the model is usually unknown, and because some restraints are usually operative so that optimum solutions exist on these critical restraint surfaces.

If, however, the restraints are never allowed to be violated during an optimization, then the resulting optimum solution is sure to be a feasible one (that is, one where no restraints are violated). Employing this concept, one can consider two competing requirements which are to be simultaneously, though somewhat compromisingly, met during optimization: (1) maximization of the effectiveness function as quickly as possible while, at all times, (2) positively avoiding violation of the restraints.

The second requirement can be satisfied by devising a penalty, becoming increasingly severe, as restraint boundaries are approached. This penalty, or cost for being too close to the restraints and thereby threatening their violation, can be subtracted from the value of the effectiveness function to give a new "control" function in exactly the same way as dollar costs are subtracted from dollar profits to give "net

profit" as a sound measure of economic effectiveness.

The resulting new function, which is really a created response function, will be called A. Let E represent the effectiveness function in a form suitable for maximization. Then, if all restraints (say there are m of them) are expressed in the form: $R_i \geq 0$, an A-function compatible with the requirements of the new approach can be written:

$$A = E - r \underbrace{\sum_{i=1}^{m} \frac{W_i}{R_i}}_{\text{penalty}} .$$

As any restraint, R_i, approaches its limiting value (zero), A approaches negative infinity. In this way, a progressively severe penalty is imposed as the boundary of a restraint is approached. (The W_i's [always >0] weight the individual penalties amongst themselves while the r [always ≥ 0] weight the sum of these penalties in relation to E.) Since the optimum solution lies on any restraint boundaries which are critical (critical R's = 0), and conceivably very close to other, near-critical restraint boundaries, it must be possible to eventually set r = 0 so that optimal solutions can reside, penalty-free, on or close to such limiting boundaries. At the same time, since A would then equal E, the true effectiveness function would be maximized.

Such an approach to restrained optimizations results in the creation of one dome-shaped A-surface, itself having a maximum, for each nonzero value of r. The modified path of ascent in Figure 4 is really the continuous projection onto the E-surface of the maxima of the

infinite set of A-surfaces created as r is continually relaxed from some positive, finite, initial value to zero. The A-surfaces all lie beneath the E-surface for $r > 0$. The larger the value of r, the greater the penalty in relation to E, and the farther below the E-surface the corresponding A-surface lies. Finally, all the A-surfaces exist entirely within the "solution space" defined by the limits of the restraints.

Suppose from some feasible starting point the Method of Steepest Ascents is used to determine the maximum on the lowest A-surface. The values of the independent variables corresponding to this maximum can be used to determine the starting point of a second maximization on the next higher A-surface (the one characterized by the next smaller value of r) and this process can be repeated until $r = 0$ ($A = E$). Then a final short ascent can be made on the E-surface until critical restraints are met. In this way not only are the restraint boundaries automatically avoided during the optimization, but successive maxima tunnel up through the solution space, in a sense being continually guided in the direction of the desired optimum.

Essentially then, this new approach is based on steepest ascents up a succession of created response surfaces, within the natural solution space. Consequently, it has been entitled the Created Response Surface Technique (CRST).

ILLUSTRATIVE EXAMPLES

Two simple applications of the CRST will more concretely illustrate the nature of the approach and the type of computations required.

EXAMPLE I

Maximize $\underline{E} = E(\underline{x}) = \underline{x}$ for $0 \leq \underline{x} \leq 1$.

Putting the restraints in the required form ($\underline{R}_i \geq 0$), the problem can be rewritten:

Maximize $\underline{E} = E(\underline{x}) = \underline{x}$, subject to

$\underline{R}_1 = \underline{x} \geq 0$, and

$\underline{R}_2 = (1 - \underline{x}) \geq 0$.

Figure 11 of this appendix illustrates the $\underline{E}$-surface, restraints, and several $\underline{A}$-surfaces corresponding to the indicated values of $\underline{r}$. The weighting factors, $\underline{W}_1$ and $\underline{W}_2$, have been somewhat arbitrarily taken to be 0.3 and 0.7, respectively. These weighting factors remain fixed during the optimization.

Let the initial feasible solution be $\underline{x} = 0.275$. The desirability of this starting condition, considering its effectiveness and proximity to restraint boundaries, is measured by the corresponding value on the lowest $\underline{A}$-surface. This is represented by the lowest dot on the $\underline{A}$-surface characterized by $\underline{r} = 0.5$ in Figure 11. Stepwise progress in the direction of steepest ascents (here, simply, the positive $\underline{x}$-direction) gives rise to dots, each higher than their predecessors, until finally a value of $\underline{x}$ (= 0.585) is reached causing $\underline{A}$ to begin to fall off (see the cross mark). Preserving the value of $\underline{x}$ corresponding to the highest point (i.e., $\underline{x}$ for the case immediately preceding the one where $\underline{A}$ was found to decrease), $\underline{r}$ is reduced arbitrarily to 0.3 and the corresponding point on the next higher $\underline{A}$-surface becomes the starting point for a similar ascent on this surface. Progress is made up this surface to the

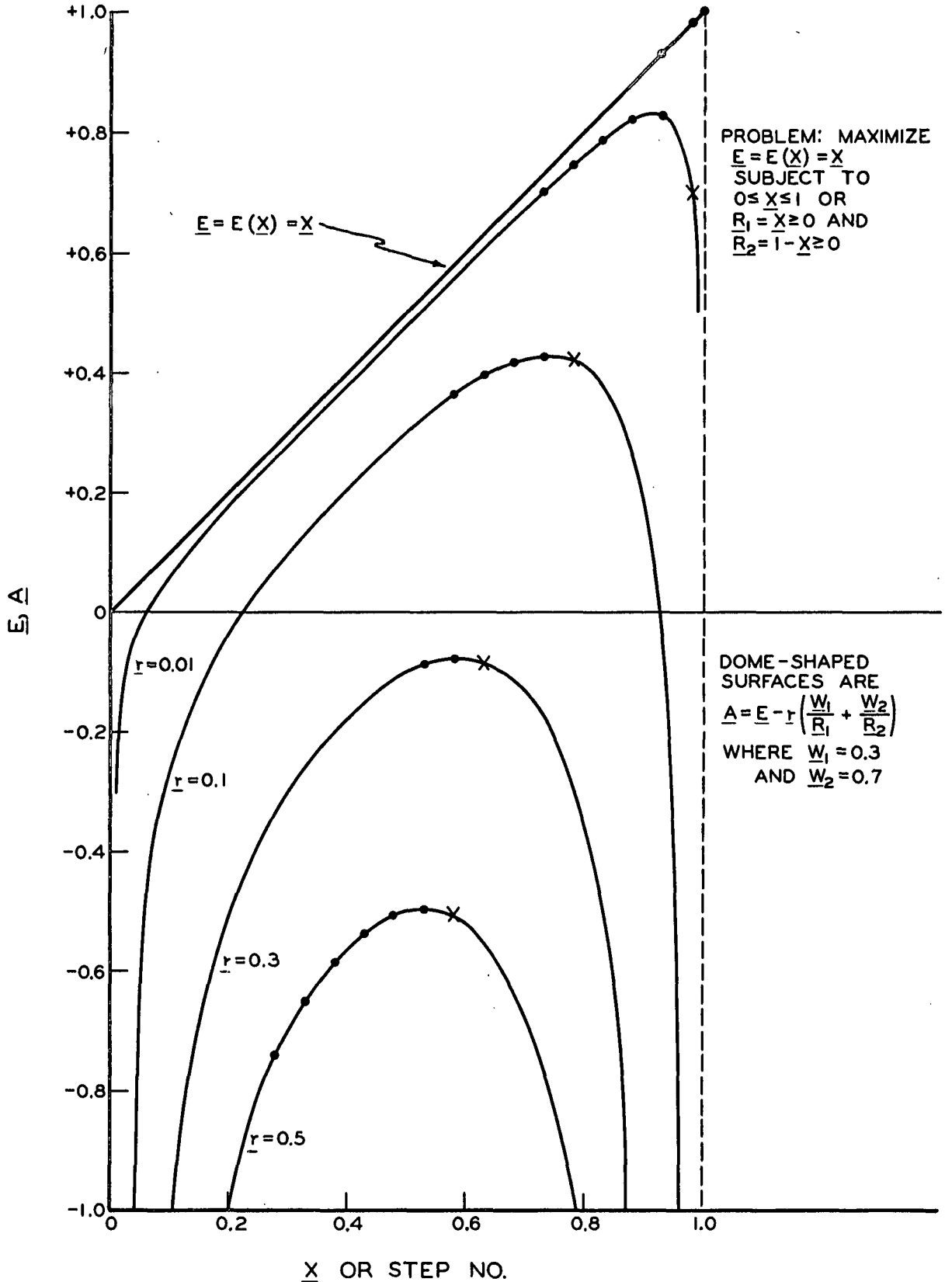

Figure 11. Effectiveness Surface and Created Response Surfaces for Example I

approximate maximum, where another jump to the next higher A-surface occurs, etc., until the jump is onto the E-surface ($r = 0$, A = E). (The number of A-surfaces involved is arbitrary.) The guidance provided by the progress up through the solution space is relied upon to bring the starting point on the E-surface very close to the optimum.

On the effectiveness surface in a general problem having more than two dimensions, progress is made in the direction of steepest ascents and not necessarily directly toward the optimum. However, if the distance travelled is small, an optimum or near optimum will result, and critical restraints will be zero or very small. In order to press closer into the optimum "corner," reduction of step size at this final stage is very desirable.

Figure 12 is a simplified logic diagram showing an automatic digital computer program compatible with the Created Response Surface concept and allowing for ultimate optimization.

EXAMPLE II

$$\text{Maximize } E = \sqrt{25 - (x - 5)^2 - (y - 5)^2} \text{ , subject to*}$$

$$R_1 = (0.8)\,x - y \geq 0, \text{ and}$$

$$R_2 = 8 - (0.8)\,x - y \geq 0.$$

Here, the effectiveness function is the equation of a sphere having a radius of 5 and having its center at $x = 5$, $y = 5$, $E = 0$. The restraints are planes, running parallel to the E-axis and intersecting

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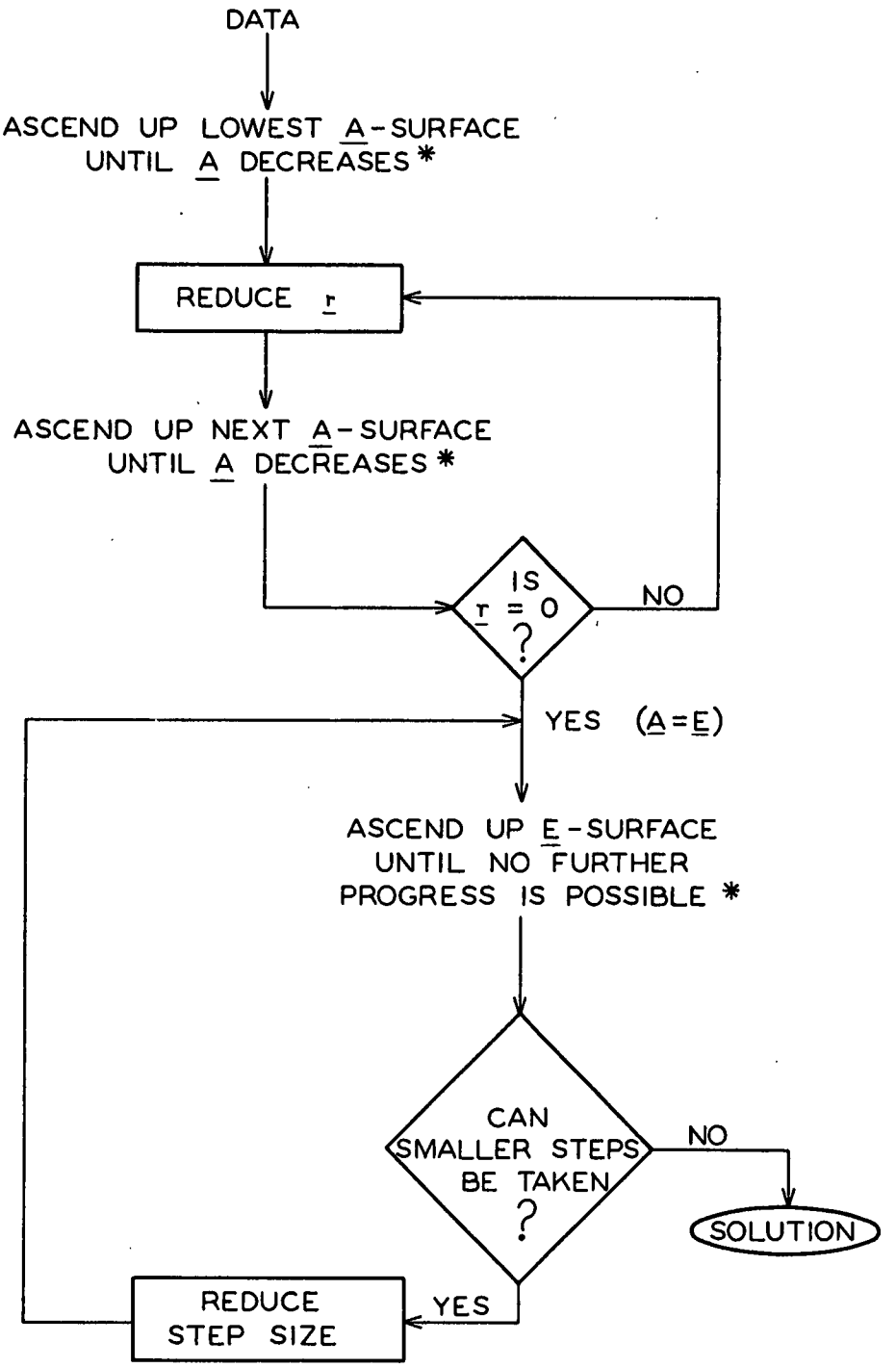
* The restraint functions as written measure the distance of a point in the solution space from the restraint boundaries in the y-direction. They could have been expressed in terms of the x-direction. The choice appears to be unimportant. However, see Appendix VIII for more on this point.



* IN TAKING STEPS IN ANY ASCENT RESTRAINTS MUST NOT BE VIOLATED

Figure 12. Simplified Logic Diagram Compatible With the CRST

the sphere and each other. Figure 13 is a contour diagram of the effectiveness function; it also shows the restraints and the path ultimately followed in applying the CRST (heavy solid line through data points). The arrows from the restraint surfaces point in the direction of allowable solution. The solution space is seen to be a triangular wedge in the lower portion of the figure.

The actual optimum occurs at the intersection of the two restraint surfaces on the effectiveness surface. This maximal $\underline{E}$ can be easily determined (at $\underline{x} = 5$, $\underline{y} = 4$) to be 4.899. However, to further illustrate the nature of the new approach, the CRST will again be used to seek an approximate optimum. In addition, this example will show the kind of computations which are required in typical, realistic applications (e.g., see Appendix VI).

The created response surface equations are given generally by

$$\underline{A} = \underline{E} - \underline{r} \sum_{\underline{i}} \frac{\underline{W_i}}{\underline{R_i}}. \qquad (33)$$

For this particular problem, letting $\underline{W_1} = 3.6$ and $\underline{W_2} = 0.4$:

$$\underline{A} = \sqrt{25 - (\underline{x} - 5)^2 - (\underline{y} - 5)^2} - \underline{r}\left[\frac{3.6}{(0.8)\underline{x} - \underline{y}} + \frac{0.4}{8 - (0.8)\underline{x} - \underline{y}}\right]. \qquad (84)$$

The path of steepest ascents up a response surface is the one resulting from progress always in the direction of the gradient of the function describing that surface. If $\phi(\underline{x},\underline{y},\underline{z}...)$ represents such a function, its gradient is:

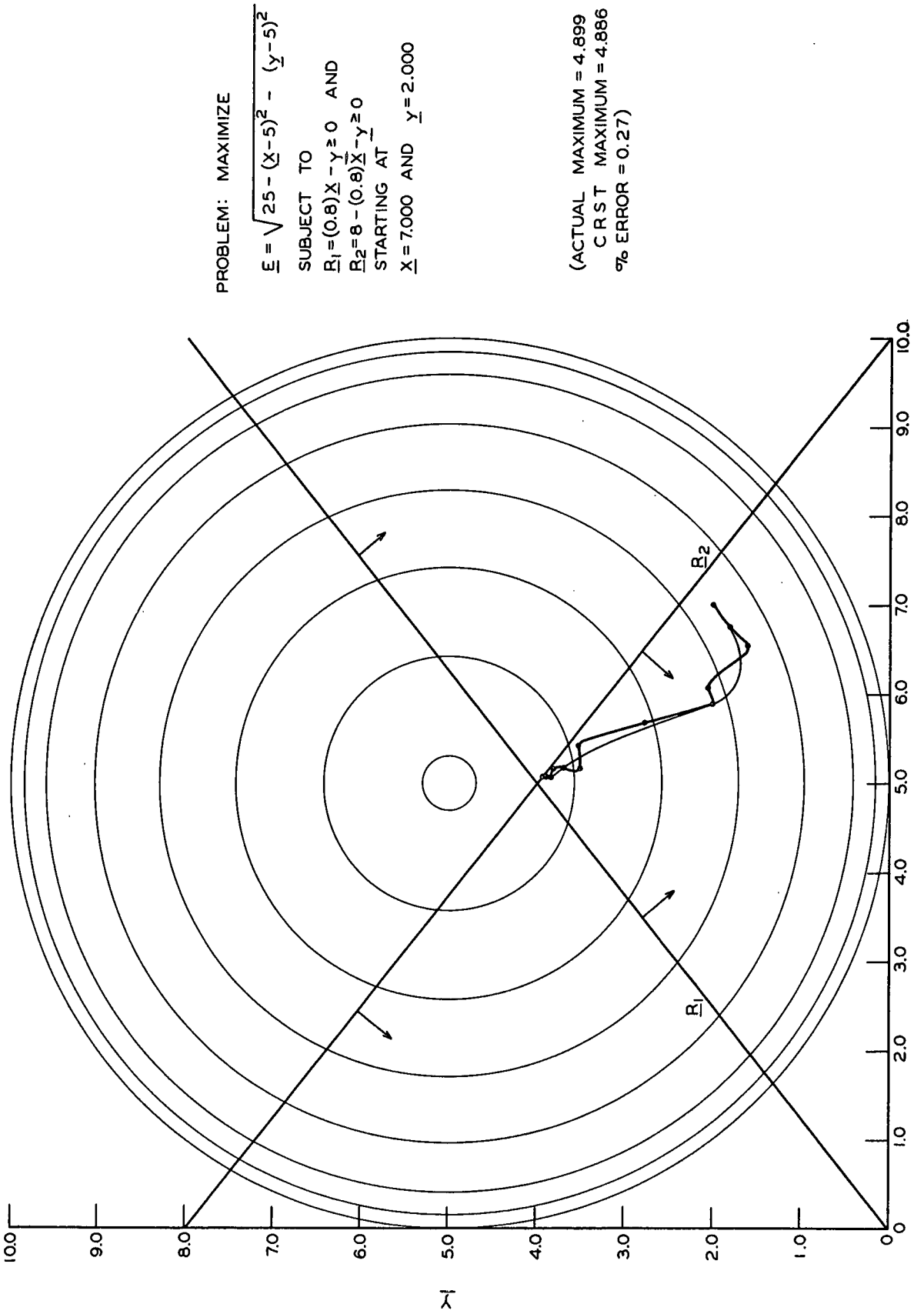


Figure 13. Contour Diagram, Restraints, and Ascent Paths for Example II

$$\nabla\phi = \frac{\partial\phi}{\partial \underline{x}}\,\bar{\underline{i}} + \frac{\partial\phi}{\partial \underline{y}}\,\bar{\underline{j}} + \frac{\partial\phi}{\partial \underline{z}}\,\bar{\underline{k}} + \ldots.$$

Here $\bar{\underline{i}}$, $\bar{\underline{j}}$, $\bar{\underline{k}}$, etc. are unit vectors in the $\underline{x},\underline{y},\underline{z},\ldots$ direction.

To move in the direction of the gradient, it is only necessary to continually and simultaneously adjust the independent variables by amounts proportional (by the same proportionality constant) to their respective components as given in the gradient expression. Thus, to move in the direction of steepest ascents in the ϕ-surface (that is, to increase ϕ at the maximum rate), $\underline{x},\underline{y},\underline{z}$, etc. would be changed simultaneously by an amount proportional to $\partial\phi/\partial\underline{x}$, $\partial\phi/\partial\underline{y}$, $\partial\phi/\partial\underline{z}$, etc., respectively.

In actual computations, the gradient is not continually calculated. At a given starting point, the components of a base gradient are calculated or approximated. Then after choosing a proportionality constant, $\underline{h}$, the independent variables are adjusted by adding $\underline{h}$ times the appropriate gradient component (or its approximation) to the base value of the corresponding variable. Thus, if the base value of $\underline{x}$ is $\underline{x}_b$, the new value of $\underline{x}$ becomes $\underline{x}_b + \underline{h}\left.\frac{\partial\phi}{\partial\underline{x}}\right|_{\underline{x}_b,\,\underline{y}_b,\,\underline{z}_b,\ldots}$

If the new value of each variable is calculated and a new ϕ computed using these new values, ϕ will be increasing at approximately its greatest spatial rate.

The direction of steepest ascent so calculated is generally exact only at the base point (and there, only when the components of the gradient are not approximated). Thus, continued steps in this direction may deviate considerably from those corresponding to the true path of steepest ascent, especially when the response surface is complicated.

The choice of step size and of how far to progress on a given ascent is somewhat arbitrary. A good general rule on the extent of an ascent seems to be to progress in the direction of a given base gradient until the value of the response starts to fall off (13). However, see (50) and Appendix VI. Here one can go back to the best case (that is, the case for the immediately preceding conditions) and calculate a new gradient using these conditions as a new base. A given response surface can be ascended in this "zig-zag" manner until, following the calculation of a new base case, not even one, small, first step can be taken. At this point it may be assumed that the maximum of the response surface is nearby. [This may not always be the case. The problems of level surfaces, alternate optima, etc., are discussed in (10, 13).] It is at this stage, in the CRST, that the value of $\underline{r}$ is reduced and a new $\underline{A}$-surface is ascended. When, after a number of ascents, $\underline{r}$ finally becomes zero, a final, short ascent on the true effectiveness surface should lead to a solution very close to the actual optimum.

In the present example, the components of the gradient can be easily calculated by partial differentiation of the expression for $\underline{A}$, Equation (84).[a] Thus:

$$\frac{\partial \underline{A}}{\partial \underline{x}} = \frac{5 - \underline{x}}{\underline{E}} + \underline{r}\left[\frac{2.88}{(\underline{R}_1)^2} - \frac{0.32}{(\underline{R}_2)^2}\right]$$

and

$$\frac{\partial \underline{A}}{\partial \underline{y}} = \frac{5 - \underline{y}}{\underline{E}} - \underline{r}\left[\frac{3.6}{(\underline{R}_1)^2} + \frac{0.4}{(\underline{R}_2)^2}\right].$$

[a] These components may be approximated too. Thus, the component, $\partial \underline{A}/\partial \underline{x}$, could have been approximated by $[(\Delta \underline{A})_{\underline{x}}/\Delta \underline{x}]_{\underline{y}}$: that is, the change in $\underline{A}$ $(\Delta \underline{A})_{\underline{x}}$ produced by a small, arbitrary change in $\underline{x}$ $(\Delta \underline{x})$, $\underline{y}$ being held constant at its base value. See (13) and Appendix VI for application of this approximation method.

Starting this illustrative optimization at, say, $\underline{x} = 7$, $\underline{y} = 2$, as an initial, feasible solution,

$$\left.\frac{\partial \underline{A}}{\partial \underline{x}}\right|_{\substack{\underline{x}=7 \\ \underline{y}=2}} = -2.355$$

$$\left.\frac{\partial \underline{A}}{\partial \underline{y}}\right|_{\substack{\underline{x}=7 \\ \underline{y}=2}} = -1.912^{a}$$

For $\underline{r} = 1$ and $\underline{h} = 0.1$, a first ascent can be taken (see Table XIII) starting at the initial conditions mentioned above. The new values of $\underline{x}$ and $\underline{y}$ for the first step of this first ascent are

$$\underline{x} = 7.000 + 0.1(-2.355)$$
$$= 7.000 - 0.236 = 6.764$$

and

$$\underline{y} = 2.000 + 0.1(-1.912)$$
$$= 2.000 - 0.191 = 1.809.$$

From these values, $\underline{R}_1$, $\underline{R}_2$, $\underline{E}$, the penalty, and $\underline{A}$ can be calculated and are shown in the table. Other steps for this first ascent are calculated in a similar manner.

---

[a] Using $\Delta\underline{x} = \Delta\underline{y} = 0.01$, the approximate components of the gradient are

$$\left[\frac{(\Delta \underline{A})_{\underline{x}}}{\Delta \underline{x}}\right]_{\underline{y}} = -2.398 \text{ and } \left[\frac{(\Delta \underline{A}_{\underline{y}})}{\Delta \underline{y}}\right]_{\underline{x}} = -1.979.$$

The exact calculations of the components of the gradients will be used here and throughout the rest of this example. (The approximate technique is used in optimizing the hypothetical kraft pulping system. See Appendices VI and VII.)

TABLE XIII
CALCULATIONS FOR EXAMPLE II[a]

	1st Ascent, r = 1.0				2nd Ascent, r = 1.0			3rd Ascent, r = 1.0			4th Ascent, r = 1.0	
	Initial Base	1	2*	③	Base	1*	②	Base	1*	②	Base*	①
Cumulative step no. (see Fig. 14)	1	2	3			4			5			
h	——	0.1	→	→	——	1.0	→	——	1.0	→	——	2.0
x	7.000	6.764	6.528	6.292	6.528	6.056	5.584	6.056	5.890	5.724	5.890	5.832
y	2.000	1.809	1.618	1.427	1.618	2.053	2.488	2.053	2.018	1.983	2.018	2.054
$\partial A/\partial x$	-2.355	→	→	→	-0.472	→	→	-0.166	→	→	-0.029	→
$\partial A/\partial y$	-1.912	→	→	→	+0.435	→	→	-0.035	→	→	+0.018	→
R_1	3.600	3.602	3.604	3.607	3.604	2.792	1.979	2.792	2.694	2.596	2.694	2.612
R_2	0.400	0.780	1.160	1.539	1.160	1.102	1.045	1.102	1.270	1.438	1.270	1.280
E	3.464	3.421	3.351	3.250	3.351	3.899	4.284	3.899	3.914	3.921	3.914	3.953
$r\sum_i \frac{W_i}{R_i}$	2.000	1.512	1.344	1.258	1.344	1.652	2.202	1.652	1.651	1.665	1.651	1.691
A	1.464	1.909	2.007	1.992	2.007	2.247	2.082	2.247	2.263	2.256	2.263	2.262

[a] See text of Appendix V for significance of starred and encircled step numbers.

The value of A falls off from the previous value at step 3 (encircled) and thus step 2 (marked by an asterisk) becomes the base for the calculation of another ascent where h is now taken to be 1.0. In a similar manner, a third ascent is taken. Finally, in attempting a further ascent, not even a first step can be taken with h = 2.0 without A decreasing. It is assumed, therefore, that the maximum of the lowest A-surface is close by, and thus the value of r is reduced, arbitrarily, to 0.01. The first portion of Table XIV indicates the conditions for and the results of the subsequent ascents. (Notice that the third step of the first ascent leads to a restraint violation so that the step size (h) is reduced for step 4, which is feasible.) The attempted fourth ascent indicates a further reduction of r. This time, r is set equal to 0.001 (see Table XV). After four ascents on this A-surface characterized by r = 0.001, r is allowed to equal zero and A = E. The final ascent (right hand portion of Table XV) arrives at the approximate optimum of 4.886. This is only 0.27% below the true optimum of 4.899. By making r very, very small, by calculating the gradient very accurately if an approximation is used, and by employing extremely small values of h, the difference between the optimum obtained by means of the CRST and the true optimum can be made as small as desired.

Figure 13 indicates the path connecting the calculated (approximate) maxima for the various ascents (thick solid line through data points). The thin solid line is the approximate path that would result if the A-surface maxima were projected onto the E-surface as r was continuously relaxed to zero. Note in Figure 13 (also see Table XIII, and Figure 14, to be discussed) that at first E actually decreases to allow for an initial movement away from restraint R_2. This decrease in

TABLE XIV
CALCULATIONS FOR EXAMPLE II[a]

	1st Ascent, r = 0.01					2nd Ascent, r = 0.01			3rd Ascent, r = 0.01			4th Ascent, r = 0.01	
	Base	1	2*	3	④	Base	1*	②	Base	1*	②	Base*	①
Cumulative step no. (See Fig. 14)	(5)	6	7				8			9			
h	——	1.0	→		0.2	——	1.0	→	——	1.0	0.5	——	1.0
x	5.890	5.665	5.440	5.215	5.395	5.440	5.175	4.910	5.175	5.185	5.190	5.185	5.152
y	2.018	2.772	3.526	4.280	3.677	3.526	3.514	3.502	3.514	3.700	3.793	3.700	3.617
$\partial A/\partial x$	-0.225	→				-0.265	→		+0.010	→		-0.033	→
$\partial A/\partial y$	+0.754	→				-0.012	→		+0.186	→		-0.083	→
R_1	2.694	1.760	0.826	-0.108	0.639	0.826	0.626	0.426	0.626	0.448	0.359	0.448	0.505
R_2	1.270	0.696	0.122		0.007	0.122	0.346	0.570	0.346	0.152	0.055	0.152	0.261
E	3.914	4.427	4.758		4.806	4.758	4.771	4.769	4.771	4.825	4.848	4.825	4.803
$r\sum_i \frac{W_i}{R_i}$	0.017	0.026	0.076		0.628	0.076	0.069	0.092	0.069	0.107	0.173	0.107	0.087
A	3.897	4.401	4.682		4.178	4.682	4.702	4.677	4.702	4.718	4.675	4.718	4.716

[a] See text of Appendix V for significance of starred and encircled step numbers.

TABLE XV
CALCULATIONS FOR EXAMPLE II[a]

	1st Ascent, $r = 0.001$			2nd Ascent, $r = 0.001$			3rd Ascent, $r = 0.001$			4th Ascent, $r = 0.001$		Final Ascent, $r = 0$; $A = E$		
	Base	1*	②	Base	1*	②	Base	1*	②	Base*	①	Base	1	2
Cumulative step no. (See Fig. 14)	(9)	10			11			12				(12)	13	14
h	———	0.5	0.2	———	0.7	0.3	———	0.3	0.2	———	1.0	———	0.2	0.05
x	5.185	5.166	5.158	5.166	5.073	5.033	5.073	5.077	5.080	5.077	5.048	5.077	5.074	5.073
y	3.700	3.817	3.864	3.817	3.851	3.865	3.851	3.882	3.903	3.882	3.873	3.882	3.928	3.939
$\partial A/\partial x$	-0.038	→	→	-0.133	→	→	+0.014	→	→	-0.029	→	-0.016	→	→
$\partial A/\partial y$	+0.234	→	→	+0.048	→	→	+0.104	→	→	-0.009	→	+0.229	→	→
R_1	0.448	0.316	0.262	0.316	0.207	0.161	0.207	0.180	0.161	0.180	0.165	0.180	0.131	0.119
R_2	0.152	0.050	0.010	0.050	0.091	0.109	0.091	0.056	0.033	0.056	0.089	0.056	0.013	0.003
E	4.825	4.855	4.867	4.855	4.866	4.869	4.866	4.873	4.878	4.873	4.871	4.873	4.883	4.886
$r \sum_i \frac{W_i}{R_i}$	0.011	0.019	0.054	0.019	0.022	0.026	0.022	0.027	0.034	0.027	0.026	0	0	0
A	4.814	4.836	4.813	4.836	4.844	4.843	4.844	4.846	4.844	4.846	4.845	4.873	4.883	4.886

[a] See text of Appendix V for significance of starred and encircled step numbers.

effectiveness is more than compensated for by decreasing the penalty for being too close to restraining surfaces, so that the net effect is an increase in A. (On the other hand, in the first ascent where r = 0.01 (see Table XIV), A finally falls off in attempted step 4 because R_2 is approached too closely.)

Figure 14 plots A and E against cumulative step number. Here, of course, in contrast to "step no." in Figure 11 of the first illustrative example where only x is changed, a given step results from the simultaneous change of both independent variables involved. Note the similarity in appearance between Figure 14 and Figure 11.

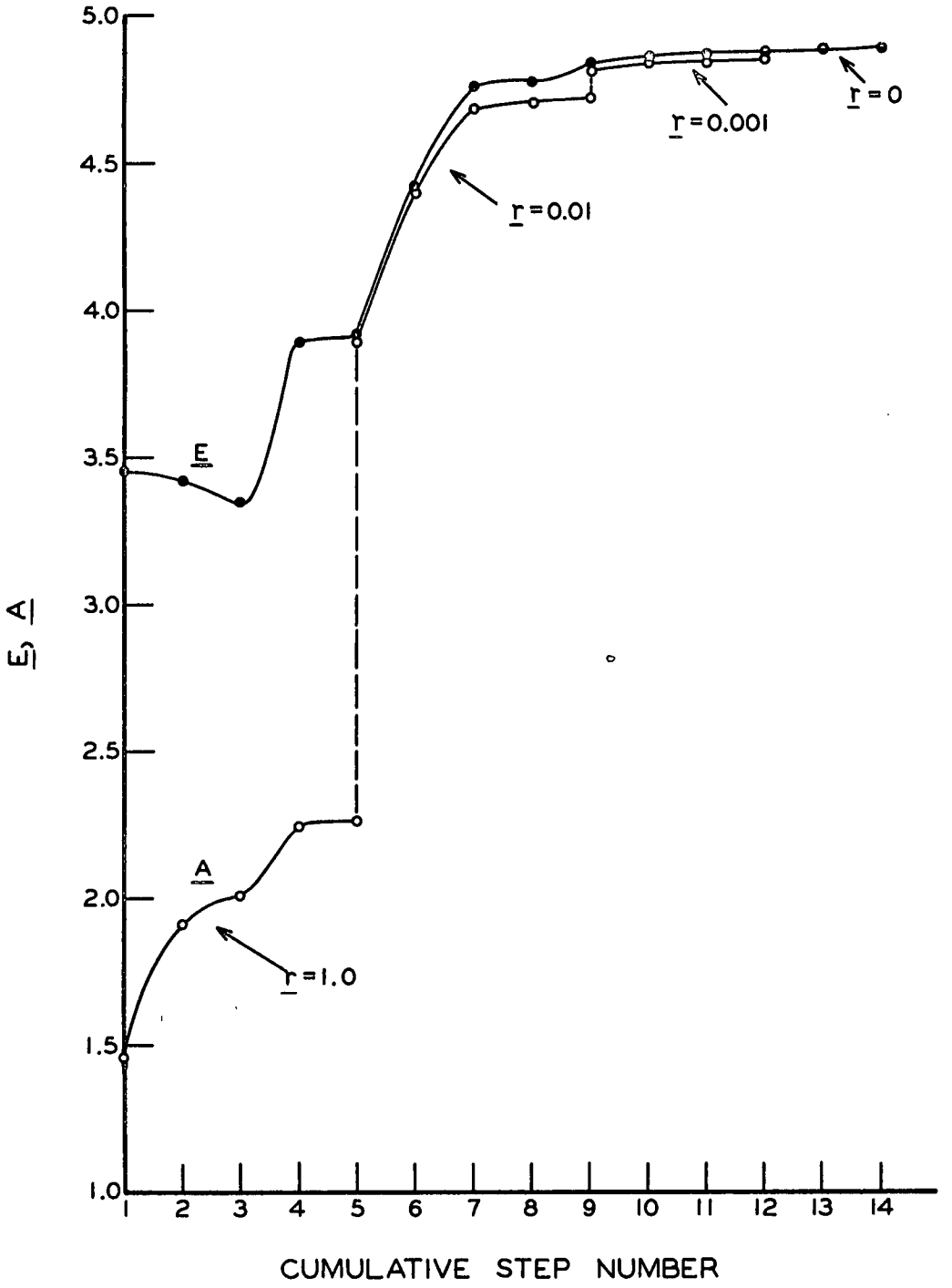


Figure 14. E, A, vs. Cumulative Step Number for Example II

APPENDIX VI.

DEVELOPMENT OF THE IBM 650 COMPUTER PROGRAM[a]

Computer programming includes all the procedures necessary in order to develop a detailed listing of "basic machine language" instructions for solving a given problem on a computer. The first step in developing a computer program for the optimization of the hypothetical kraft pulping system of this thesis was to devise a "logic diagram." A logic diagram indicates the logical decisions which must be made in connection with the calculations involved in order to apply a given solution technique (e.g., the CRST) to a given problem (e.g., optimization of the pulping system model). The logic diagram developed for optimizing the hypothetical kraft pulping system by means of the CRST is presented in Figure 15.[b] Note the basic similarity in appearance and logic to Figure 12 of Appendix V.

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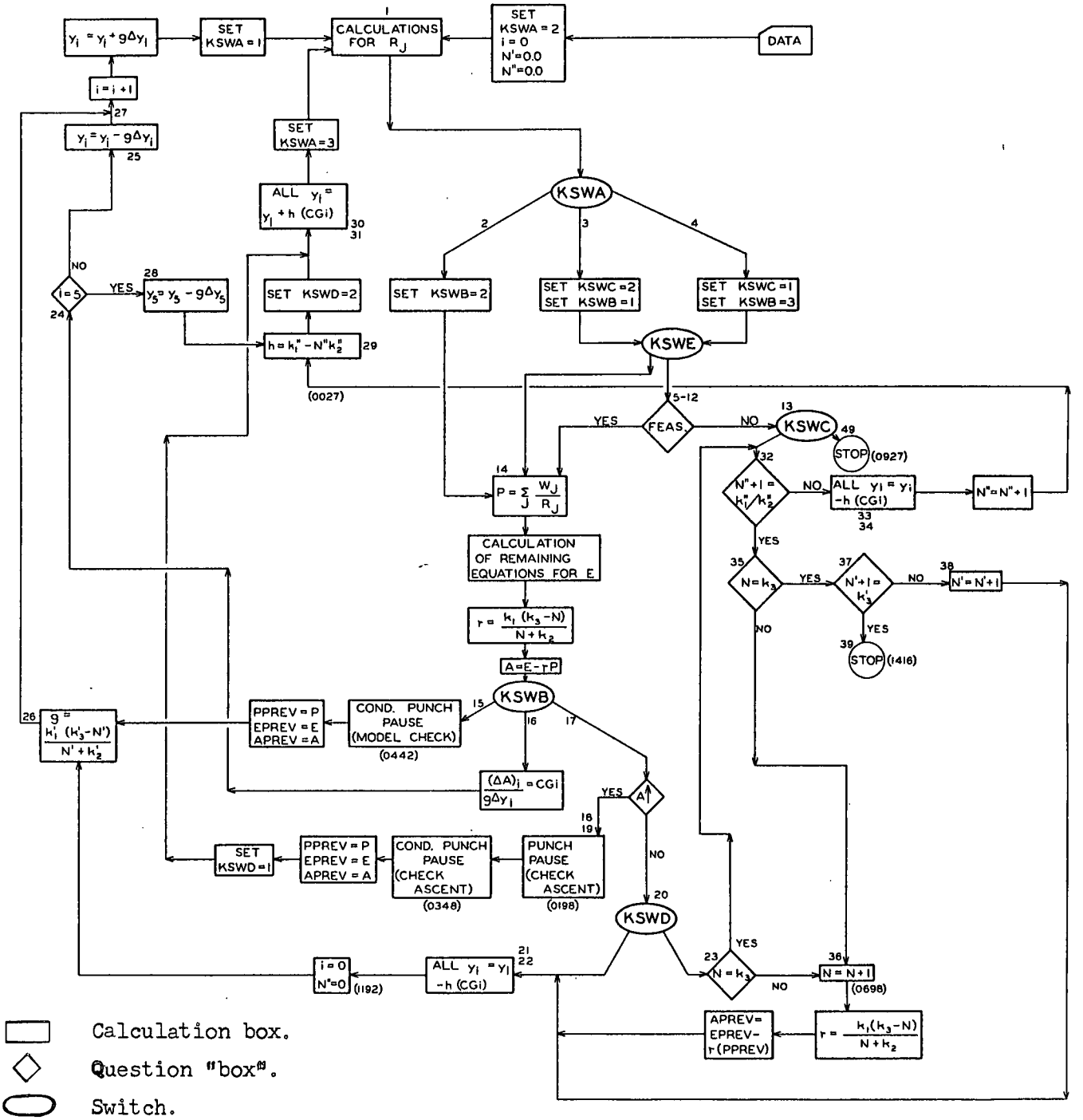
[a] For a complete description of computer programming, see, e.g., (51). For IBM 650 programming, see (52). This appendix is intended for those already familiar with IBM 650 programming.

[b] This is, potentially, a fully automatic optimization scheme. In practice, though, step size must be periodically adjusted, subjectively, in order to maintain efficient progress. Two changes (within the framework of the present logic diagram) would help to eliminate this subjective manipulation:

(1) Develop a step size reduction to allow, initially, for very large steps away from a given base. To check for overstepping a maximum, possibly changes in the signs of the gradient components would be useful. Another approach to estimating step size is to follow the rate of deviation of the linear approximation surface from the curvilinear response surface [see, e.g., (50)].

(2) Recognize formally that the step size is directly proportional to not only h, but the component of the gradients also. When these latter become small (e.g., near the top of an A-surface where $r > 0$), the value of h must be increased proportionately to keep the step size constant. However, it is precisely at this stage of an A-surface maximization that smaller steps are desirable. The difficulty of developing a general, completely



Calculation box.

Question "box".

Switch.

(0027), and other numbers in parenthesis: object program location addresses.

15, and other plain numbers: Fortran source program statement numbers.

Figure 15. Logic Diagram for Optimizing the Hypothetical Kraft Pulping System by the CRST

The next step in developing a computational program for carrying out the optimization of the pulping system model by means of the CRST was to write a "source program." A source program is a quantitative expression of the computational procedures necessary to make the calculations required according to the nature of the model and the method of solution. The source program is thus compatible with the associated logic diagram. Exhibit V lists the source program developed for the pulping system optimization. It provides for use of the IBM For Transit system, which allows for relatively easy programming, since the Fortran statements used are very much like their counterpart statements in the model.[a] This Fortran source program consists of the calculations necessary to optimize (by the strategy of Figure 15) the pulping system model by means of the CRST.

The source program was translated automatically (i.e., by the computer), in a separate operation, to a so-called "object program." The object program consists of detailed "basic machine language" instructions corresponding to the original source program statements. It is

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automatic program is apparent.

Certain other changes may be desirable. One of these, involving transferal of the PUNCH command at 0348 to a place immediately before the "up BNR one" step at 0698, would save considerable punching time.

Finally a feasibility check during gradient component approximations (this will be discussed in Appendix VIII) is desirable. This is purposely by-passed in the logic scheme of Figure 15 to save computer time.

[a] The notation used in these Fortran statements is, in some cases, slightly different from that in the logic diagram and the corresponding equations in the model [see (52) for details]. Thus, for example, $\underline{N}$ in Figure 15 and $\underline{L}_{\underline{N}}$, $\underline{K}_6$, and $\underline{n}$ (number of digesters) in Exhibit I become, respectively, BNR, ALN, AKK6, and DIGNO. A comparison of the Fortran statements with the corresponding statements in the logic diagram and the model will reveal the identity of any symbol.

EXHIBIT V: FORTRAN SOURCE PROGRAM

```
0  0000 0 DIMENSIONY(5),
0  0000 1 CG(5),DELY(5)
0  0000 0 READ,Y,DELY,AKK6,
0  0000 1 AKK7,DIGNO,AK9
0  0000 0 READ,BK1R,BK2R,BK3R,
0  0000 1 BK1G,BK2G,BK3G,
0  0000 2 BK1H,BK2H
0  0000 0 READ,KSWE,BNR
0  0000 0 READ,LW1,LW2,LW3,
0  0000 1 LW4,LW5,LW6,
0  0000 2 LW7,LW8
0  0000 0 I=0
0  0000 0 BNG=0.0
0  0000 0 BNH=0.0
0  0000 0 KSWA=2
0  0001 0 ALN=520.8/(Y(4)
0  0001 1 -192.5)+12.0
0  0000 0 X3=3.535E-4*Y(1)**2+
0  0000 1 .5311*Y(1)+8.705E-2
0  0000 2 *ALN*Y(1)
0  0000 0 X3=X3/(.052*Y(1)+78.
0  0000 1 +2.377E-3*ALN*Y(1))
0  0000 0 X2=19.*X3
0  0000 0 X1=4.782E-4*(Y(1)
0  0000 1 -X3)+1.956E-3*(Y(1)-
0  0000 2 X3)**2/Y(2)
0  0000 0 X1=(X1+6.376E-3*X2+
0  0000 1 1.594E-2*X3)/Y(2)
0  0000 0 X1=(.95-X1)*(Y(1)-X2
0  0000 1 -X3)
0  0000 0 X4=Y(1)-X1-X2-X3
0  0000 0 SUMXA=1.29*X1+1.258
0  0000 1 *X2+2.29*X3+1.71
0  0000 2 *X4
0  0000 0 VL=Y(2)+Y(3)+41.6
0  0000 0 CONC=.995*(X1+X2)
0  0000 1 /VL
0  0000 0 CHWD=.995*(X1+X2)
0  0000 1 /3798.
0  0000 0 TT=96.82/(CONC-.0663
0  0000 1 *CONC/CHWD-.3153)+
0  0000 2 .321*VL
0  0000 0 AI=3623.+64.4*Y(2)+5
0  0000 1 8.4*Y(3)+DIGNO*3.657
0  0000 2 8E4/(TT+Y(5))
0  0000 0 AL=.995*SUMXA+1998.-
0  0000 1 1.75*ALN
0  0000 0 S=AL/(.995*SUMXA+60.
0  0000 1 8*Y(2)+48.*Y(4)-.112
0  0000 2 1*AI-5095.)
0  0000 0 CE=1.48E5-3.31E5*S
0  0000 1 +40.*AL-61.*S*AL
0  0000 0 R1=10.-1.103E-2*Y(1)
0  0000 0 R2=X2-.389*X1
0  0000 0 R3=1.5*Y(2)-Y(3)
0  0000 0 R4=VL-213.1
0  0000 0 R5=Y(5)-25.
0  0000 0 R6=AKK6-3496.*ALN
0  0000 1 /(.995*SUMXA+1998.)
0  0000 0 R7=AKK7-CE
0  0000 0 R8=DIGNO*1.5553E4/
```

EXHIBIT V: FORTRAN SOURCE PROGRAM (Continued)

```
0  0000 1 (TT+Y(5))-110.6-VL
0  0000 0 GOTO(2,3,4),KSWA
0  0000 0 PAUSE
0  0002 0 KSWB=2
0  0000 0 GOTO14
0  0003 0 KSWB=1
0  0000 0 KSWC=2
0  0000 0 GOTO(14,5),KSWE
0  0000 0 PAUSE
0  0004 0 KSWB=3
0  0000 0 KSWC=1
0  0000 0 GOTO(14,5),KSWE
0  0000 0 PAUSE
0  0005 0 IF(R1)13,13,6
0  0006 0 IF(R2)13,13,7
0  0007 0 IF(R3)13,13,8
0  0008 0 IF(R4)13,13,9
0  0009 0 IF(R5)13,13,10
0  0010 0 IF(R6)13,13,11
0  0011 0 IF(R7)13,13,12
0  0012 0 IF(R8)13,13,14
0  0013 0 GOTO(32,49),KSWC
0  0000 0 PAUSE
0  0014 0 P=LW1/R1+LW2/R2+
0  0014 1 LW3/R3+LW4/R4+LW5/R5
0  0000 0 P=P+LW6/R6+LW7
0  0000 1 /R7+LW8/R8
0  0000 0 SUMXS=1.71*Y(1)-.452
0  0000 1 *X2+.58*X3
0  0000 0 H=ALN*(2324.*SUMXA
0  0000 1 -2.874E7)/(.995*SUMX
0  0000 2 A+1998.)
0  0000 0 H=H+1.413E7-
0  0000 1 1328.*SUMXA-531.*SUM
0  0000 2 XS
0  0000 0 AM=.01635*Y(1)+
0  0000 1 1.75*ALN*.995*Y(1)/
0  0000 2 (.995*SUMXA+1998.)
0  0000 0 E=-(AL/S-AL/.52)*
0  0000 1 1.0E-4/(1.104-(.72
0  0000 2 *S))-.1365
0  0000 0 E=E+5.843E-7*H-1.17E
0  0000 1 -4*AI-2.358E-5*AL
0  0000 0 E=E-1.502E-6*CE-3.21
0  0000 1 E-2*AM-5.08E-4*X1-
0  0000 2 4.77E-3*AK9*X1
0  0000 0 E=E-37.48*ALN/(.995
0  0000 1 *SUMXA+1998.)
0  0000 0 BR=BK1R*(BK3R-BNR)
0  0000 1 /(BNR+BK2R)
0  0000 0 A=E-BR*P
0  0000 0 GOTO(15,16,17),KSWB
0  0000 0 PAUSE
0  0015 0 CONTINUE
0  0000 0 PUNCH,X1,X2,X3,X4,
0  0000 1 SUMXA,SUMXS,AM
0  0000 0 PUNCH,VL,CONC,CHWD,
0  0000 1 TT,AI,AL,ALN
0  0000 0 PUNCH,S,CE,R1,R2,
0  0000 1 R3,R4,R5
0  0000 0 PUNCH,R6,R7,R8,H,
```

EXHIBIT V: FORTRAN SOURCE PROGRAM (Continued)

```
0  0000 1 P,E,A
0  0000 0 PAUSE
0  0000 0 PPREV=P
0  0000 0 EPREV=E
0  0000 0 APREV=A
0  0000 0 GOTO26
0  0016 0 CG(I)=(A-APREV)/
0  0016 1 (BG*DELY(I))
0  0000 0 GOTO24
0  0017 0 IF(A-APREV)20,20,18
0  0018 0 CONTINUE
0  0000 0 BG=BG
0  0019 0 PUNCH,A,APREV,E,
0  0019 1 EPREV,BR,BG,BH
0  0000 0 PAUSE
0  0000 0 PUNCH,Y,CG
0  0000 0 PUNCH,X1,X2,X3,X4
0  0000 0 PUNCH,SUMXA,AM,VL,
0  0000 1 CONC,CHWD,TT,AL
0  0000 0 PUNCH,ALN,S,CE,R1,
0  0000 1 R2,R3,R4
0  0000 0 PUNCH,R5,R6,R7,R8,
0  0000 1 P,PPREV,H
0  0000 0 PUNCH,SUMXS,AI
0  0000 0 PAUSE
0  0000 0 PPREV=P
0  0000 0 EPREV=E
0  0000 0 APREV=A
0  0000 0 KSWD=1
0  0000 0 GOTO30
0  0020 0 GOTO(21,23),KSWD
0  0000 0 PAUSE
0  0021 0 DO22J=1,5,1
0  0022 0 Y(J)=Y(J)-BH*CG(J)
0  0000 0 I=1
0  0000 0 BNH=0.0
0  0000 0 GOTO26
0  0023 0 IF(BNR-BK3R)36,32,36
0  0024 0 IF(I-5)25,28,25
0  0025 0 Y(I)=Y(I)-BG*DELY(I)
0  0000 0 GOTO27
0  0026 0 BG=BK1G*(BK3G-BNG)
0  0026 1 /(BNG+BK2G)
0  0027 0 I=I+1
0  0000 0 Y(I)=Y(I)+BG*DELY(I)
0  0000 0 KSWA=1
0  0000 0 GOTO1
0  0028 0 Y(5)=Y(5)-BG*DELY(5)
0  0029 0 BH=BK1H-BNH*BK2H
0  0000 0 KSWD=2
0  0030 0 DO31J=1,5,1
0  0031 0 Y(J)=Y(J)+BH*CG(J)
0  0000 0 KSWA=3
0  0000 0 GOTO1
0  0032 0 IF(BNH+1.-BK1H/BK2H)
0  0032 1 33,35,33
0  0033 0 DO34J=1,5,1
0  0034 0 Y(J)=Y(J)-BH*CG(J)
0  0000 0 BNH=BNH+1.
0  0000 0 GOTO29
0  0035 0 IF(BNR-BK3R)36,37,36
```

EXHIBIT V: FORTRAN SOURCE PROGRAM (Continued)

```
0   0036 0 BNR=BNR+1.
0   0000 0 BR=BK1R*(BK3R-BNR)
0   0000 1 /(BNR+BK2R)
0   0000 0 APREV=EPREV-BR*
0   0000 1 PPREV
0   0000 0 GOTO21
0   0037 0 IF(BNG+1.-BK3G)
0   0037 1 38,39,38
0   0038 0 BNG=BNG+1.
0   0000 0 GOTO21
0   0039 0 STOP
0   0049 0 STOP
0   0000 0 END
```

this object program which, when "loaded" into the computer and supplied with data (see Appendix VII) to initiate computation, allows the desired optimization to be accomplished. The optimization program followed by the computer is implicit in the calculations and routes indicated on the logic diagram.

APPENDIX VII.

DISCUSSION OF DATA INPUT AND RESULTS OF THE OPTIMIZATION STUDIES

Table XVI of this appendix indicates the data (input to the computer to initiate an optimization) and some results for eight optimization runs. These data were selected to

(1) allow a validity check of the computer program,

(2) provide for some specific results from the optimization of the hypothetical kraft pulping system, and

(3) enable conclusions to be drawn concerning the use of the CRST in the optimization of other restrained systems (see Appendix VIII).

Two models of hypothetical kraft pulping systems were considered. The change from the first model to the second was effected by selection of four new values for the adjustable parameters.

Other changes from run to run included

(1) changes in the values of the $\underline{Y}$'s,

(2) changes in the $\underline{r}$-reduction schedule,

(3) changes in the accuracy of the gradient component calculations, and

(4) changes in the values of the individual restraint weighting factors, $\underline{W_i}$.

Changes in step size were made subjectively during the optimizations according to the progress made and the current magnitude of the gradient components.

DISCUSSION OF THE DATA ENTRIES

The DELY's (Table XVI), along with a calculated quantity ($\underline{g} \equiv BG$) are used in creating changes in the $\underline{Y}$'s for calculation of the approximate

TABLE XVI
DATA INPUT AND SOME RESULTS FOR OPTIMIZATION RUNS

Data \ Run	First Model[a] 1	2	Second Model[a] 3	4	5	6	7	8
Y1	752.3	688.4	900.0	→	→	→	873.2	900.0
Y2	124.3	107.4	80.0	→	→	→	83.2	80.0
Y3	83.3	81.1	115.0	→	→	→	111.1	115.0
Y4	323.0	270.9	267.0	→	→	→	268.9	267.0
Y5	30.0	40.4	27.0	→	→	→	27.7	27.0
DELY1	10.0	→	→	→	→	→	→	→
DELY2	5.0	→	→	→	→	→	→	→
DELY3	5.0	→	→	→	→	→	→	→
DELY4	7.0	→	→	→	→	→	→	→
DELY5	3.0	→	→	→	→	→	→	→
AKK6	28.0	→	21.0	→	→	→	→	→
AKK7	180,000.	→	140,000.	→	→	→	→	→
DIGNO	5.	→	4.	→	→	→	→	→
AK9	0.40	→	0.80	→	→	→	→	→
BK1R	0.1	→	→	0.0091	→	0.0002	0.002	→
BK2R	1.0	→	→	0.0910	→	→	→	→
BK3R	10.0	→	→	→	→	→	→	→
BK1G	0.350	0.042	0.0042	→	→	0.00042	0.0042	→
BK2G	3.500	0.210	→	→	→	→	→	→
BK3G	10.000	5.000	→	→	→	→	→	→
BK1H	1.0	100.0	10.0	1.0	0.1	10.0	0.10	10.0
BK2H	0.1	10.0	1.0	0.1	0.01	1.0	0.01	1.0
KSWE	2	→	→	→	→	→	→	→
BNR	0.0	9.0	0.0	→	→	→	9.0	0.0
LW1	2	→	→	→	→	→	→	→
LW2	37	→	→	→	→	→	→	→
LW3	103	→	→	→	→	→	→	→
LW4	36	→	→	→	→	→	→	→
LW5	5	→	→	→	→	→	→	→
LW6	9	→	→	1	1	9	→	→
LW7	2676	→	→	250	250	2676	→	→
LW8	68	→	→	5	5	68	→	→
Results								
Initial								
A	-6.69	2.100	→	-53.65	-53.65	→	0.951	-15.09
E	1.429	2.185	0.949	0.949	0.949	0.949	0.961	0.949
Final								
A	2.066	2.555	1.114	0.899	0.878	→	1.474	1.583
E	2.358	2.555	1.114	0.899	0.878	~0.95	1.474	1.583
Critical Restraints	R4	R3	R6	R7	R7	→	R3, R4	R6, R7, (R4)

[a] Model alterations were effected by changes in the following adjustable parameters:

Fortran Symbol	Symbol in Model, Exhibit I
AKK6	$\underline{K}_6$
AKK7	$\underline{K}_7$
DIGNO	$\underline{n}$
AK9	$\underline{k}_9$

gradient components. For example, the increased value of $\underline{Y}1$ is

$$\underline{Y}1 + \underline{g}(\text{DELY}1)$$

where

$$\underline{g} = \frac{\underline{k}_1''(\underline{k}_3'' - \underline{N}'')}{\underline{N}'' + \underline{k}_2''} \quad \text{(on logic diagram, Figure 15)}$$

or

$$\underline{g} \equiv \text{BG} = \frac{\text{BK1G}(\text{BK3G} - \text{BNG})}{\text{BNG} + \text{BK2G}}. \quad \begin{matrix}\text{(in Fortran}\\ \text{statements in}\\ \text{Exhibit V)}\end{matrix} \qquad (85)$$

A linear increase in $\underline{N}''$ ($\equiv$ BNG) causes a decrease in $\underline{g}$ ($\equiv$ BG), fast at first, then slowing. A reduced $\underline{g}$ gives more accurately calculated gradient components. The above $\underline{g}$-reduction schedule [Equation (85)] was thought to possibly reduce the number of steps required for optimization. Some other reduction schedule (perhaps in conjunction with a feasibility check--see Appendices VI and VIII) or none at all would probably have been equally good provided the gradient components were calculated accurately enough. It should be noted that the incremental changes in the $\underline{Y}$'s for gradient component calculation is dependent essentially on $\underline{g}$, and thus on Equation (85), since the DELY's are constants.

The $\underline{r}$-reduction schedule is of the same form as the $\underline{g}$-reduction schedule. Apparently, this functional form for $\underline{r}$-reduction is very desirable. (Compare successive values of $\underline{r}$ in Example II of Apppendix V.)

The step size, $\underline{h}$ ($\equiv$ BH), was reduced linearly, although as mentioned previously, BH (along with BK1H and BK2H) were adjusted

subjectively to a considerable extent. Automatic step size reduction is especially important when an optimum is being closely approached.

The value of KSWE = 2 for all runs prevented a general by-pass of the feasibility check. Such a by-pass would be useful for optimizing systems having formal restraints which are to be overlooked or which have been found to be noncritical.

The BNR has the same significance in the $\underline{r}$-reduction schedule as BNG does in the $\underline{g}$-reduction schedule of Equation (85). When BNR = 0, the optimization starts on the lowest $\underline{A}$-surface (corresponding to the largest value of $\underline{r}$). "Upping" BNR ($\equiv \underline{N}$ on the logic diagram) by ones reduces $\underline{r}$ at first quickly, then more slowly, as the optimum is approached. When BNR is upped by ones from zero to nine, the optimization progresses on ten created response surfaces ($\underline{A}$-surfaces with $\underline{r} > 0$). When BNR = 10, $\underline{r}$ = 0 since BK3R = 10; then $\underline{A} = \underline{E}$.

The LW values are the individual weighting factors ($\underline{W_i}$) for the restraints in the created response surface expression:

$$\underline{A} = \underline{E} - \underline{r} \sum_{\underline{i}} \frac{\underline{W_i}}{\underline{R_i}} . \qquad (33)$$

The particular values of the DELY's, BKR's, BKG's, BKH's and LW's were chosen more or less arbitrarily for Run 1, and adjusted according to experience or need in subsequent runs.

FIRST MODEL

RUN 1

The input values for the independent variables ($\underline{Y}$'s) in Run 1

were selected to be those for the base case of Appendix III; see also Figure 3. Because of this, the results of initial computer calculations for all the variables of the model (see Exhibit I) could be checked against the corresponding hand-computed values developed in the base case analysis. As a result of such a check, one correction in the computer program was found to be necessary. Then, a second "validity check" indicated a correctly written program.

The effectiveness of Run 1 was improved as a result of the optimization by ($2.358 - 1.429 =) $0.929 per TADP. At 250 TADP/day for a 350-day year, this improvement amounts to about $81,288 per year. This figure, of course, bears significance only in relation to the system optimized, the amount and days of production, and the starting conditions (data values for the Y's and thus the initial effectiveness).

It should be noted that Run 1 was terminated by the computational procedure before $r = 0$ (i.e., before $A = E$). This indicated a potential for still more improvement.

RUN 2

It was possible to extend Run 1 by means of Run 2 to an effectiveness of $2.555. This was done by starting at close to the best conditions of Run 1 (note values of Y's and note BNR = 9 in Table XVI), by making more accurate final gradient component calculations, and by taking smaller steps near the optimum. The corresponding improvement in effectiveness over that of the base case amounts to $98,525/year.

Restraint R3 was critical for this extended optimization. Possibly R4 instead of R3 was critical in Run 1 because of a misguiding effect caused by the somewhat inaccurately calculated gradient components,

compounded by large steps, near the maximum of the A-surface just beneath the E-surface.

SECOND MODEL

In order to study a slightly changed and more highly restrained system, the adjustable parameters were altered somewhat and a second model created. All of the runs made on this second model were characterized by more accurately calculated gradient components than in Run 2.

RUNS 3, 7, AND 8

By trial and error, initial feasible conditions were found for Run 3. Some improvement in effectiveness was made as a result of this run. It was decided to see if the "optimum" obtained in Run 3 could be improved upon. Run 7 was therefore made.

Run 7 started at the best conditions of Run 3. An r-reduction schedule, allowing much closer approach of the last A-surface (characterized by BNR = 9) to the effectiveness surface, was employed. In effect, Run 7 was an extension of Run 3, where an extra A-surface was "slipped in" between Run 3's top A-surface and the E-surface. The outcome of Run 7 showed that improvement could be made over Run 3 by allowing the A-surfaces just beneath the E-surface to press closer to this latter surface.

Run 8 was made under essentially the same initial conditions as Run 3 except that the new r-reduction schedule of Run 7 was employed from BNR = 0. That is, the whole optimization, proceeding on ten A-surfaces and the effectiveness surface, was performed from the starting point of Run 6. The results indicated considerable improvement over Run 3.

Run 8, in fact, showed improvement over Run 7, and different critical restraints were indicated. (There was a hint of R4 becoming critical in Run 8). The reason for this could be that the approximation of the maximum of the last A-surface (before the jump onto the E-surface) was made much less accurately for Run 7 than for Run 8. As a result, the ascent on the E-surface for Run 7 was actually much longer. Because the direction traveled on the E-surface is independent of the restraints, the shorter the path to the "optimum" the better. The greater chance of misdirection in Run 7 could thus explain the decreased effectiveness compared to Run 8 and the difference in critical restraints.

Run 8 represents the best run for the second model. The improvement over initial conditions was $55,475/yr. Doubtless Run 8, too, could be improved upon slightly by creating and slipping in new A-surfaces as was done in Run 7, and by taking even smaller steps on these surfaces. In retrospect, the effectiveness of Run 2 for the first model could very probably have been improved by a better r-reduction schedule and a more accurate gradient component calculation.

Further Analysis of Run 8

Table XVII shows the operating conditions for the second model before and after the optimization by Run 8. A comparison of the figures helps to reveal where and how cost economies were made in the optimization. The complexity of the pulping system and the impossibility of quantitatively determining relatively precise optimal conditions without the use of a systematic approach employing a model are apparent.

TABLE XVII

A COMPARISON OF OPERATING CONDITIONS BEFORE AND AFTER OPTIMIZATION BY RUN 8

Variable	Nature of Variable	Before	After
$X1$	NaOH	427.6	377.3
$X2$	Na_2S	258.7	228.6 288.6
$X3$	Na_2SO_4	13.6	12.0
$X4$	Na_2CO_3	200.1	139.8
ΣX_a	act. inorg. load	1250	1041
ΣX_s	smelt	1430	1199
M	make-up	23.9	20.3
V_L	tot. liq. vol.	236.6	220.9
c_i	conc.	2.886	2.729
c_w	chem./wood	0.1798	0.1587
t_t	tot. time	140.2	146.9
I	water equiv.	16,366	15,371
ℓ	BLS load	3209	3002
L_N	inorg. washer loss	19.0	18.2
s	wt.frac.sol. in BL to evaptrs.	0.2675	0.2495
C_e	cost of evaporators	135,436	139,815
$R1$	restraint	0.073[0]	1.64
$R2$	restraint	92.3	81.8
$R3$	restraint	5.0	8.1
$R4$	restraint	23.5	7.8
$R5$	restraint	2.0	4.7
$R6$	restraint (critical)	0.52	0.00087
$R7$	restraint (critical)	4564	185
$R8$	restraint	24.8	20.8
H	heat	1.156×10^7	1.195×10^7
P	penalty	73.0	0
E	effectiveness	0.949	1.583
A	created resp. function	-15.09	1.583
$Y1$	inorg. load as Na_2O	900.0	757.7
$Y2$	volume WL	80.0	75.0
$Y3$	volume BL	115.0	104.3
$Y4$	g.p.m. wash water	267.0	276.2
$Y5$	time between cooks	27.0	29.7

Figure 16 traces the changes in $\underline{E}$ and $\underline{A}$ during optimization of the second model by Run 8, using the CRST. Notice the progress on the ten $\underline{A}$-surfaces and the $\underline{E}$-surface. Also, note the similarity in appearance of Figure 16 and Figure 14 for Example II of Appendix V.

RUNS 4 AND 5

Runs 4 and 5 were essentially the same and give about the same results. They were made to determine the effect of reducing LW values for critical restraints. Weighting factors LW6, LW7, and LW8 were reduced to about one-tenth of their original values and the optimizations made. It should be noted that an improved $\underline{r}$-reduction schedule was employed in Runs 4 and 5. The result of optimizing under conditions of decreased weighting factors corresponding to critical restraints was a premature "optimum," far below that demonstrated (e.g., by Run 8) to be possible. The proposed reason for this is that the optimization was allowed to progress too closely to the critical restraints and, under the conditions of the optimization (primarily the current step sizes used), these restraints could easily be violated. The program would then reduce itself down to a final solution without being able to make further progress (see the logic diagram, Figure 15). That this actually happened was determined by "interrogating" the computer (e.g., setting the control switch to "address stop" and selecting 0027 on the address selection switches of the console).

The effect of decreasing LW7 was probably augmented because the functional form and magnitude of the quantities involved in $\underline{R}7$ resulted in its having a tremendous range of values. Thus, $\underline{R}7$ probably should have been written $1 - (\underline{C}_e/\underline{K}_7)$, rather than $\underline{K}_7 - \underline{C}_e$.

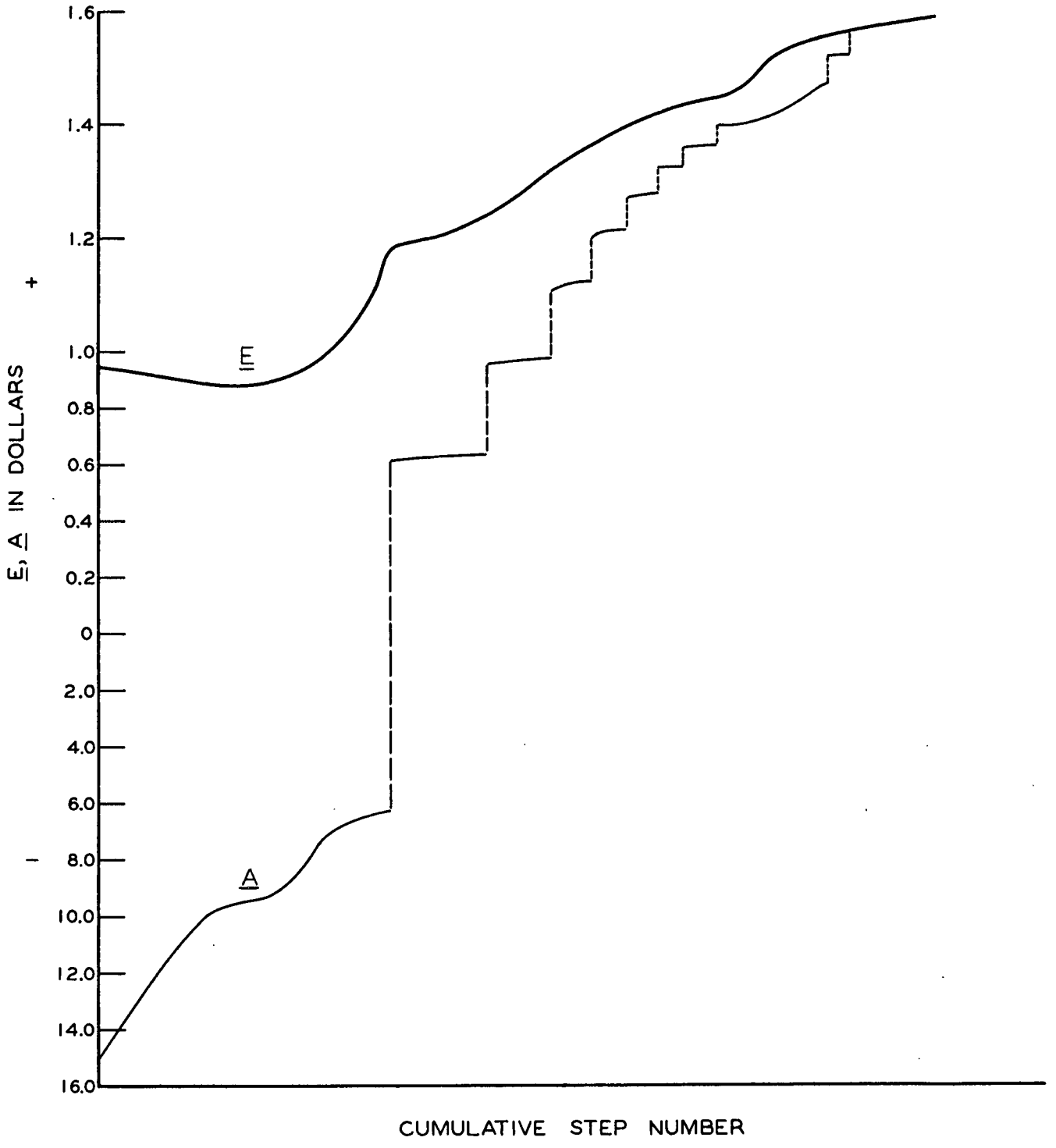

Figure 16. E, A vs. Cumulative Step Number for Run 8

RUN 6

The reduced LW values were restored to their original, though arbitrary, values after Run 5. Run 6 was made under the same initial conditions as Run 3 except that an even less approximate gradient component calculation and an r-reduction schedule, which pressed all A-surfaces very much closer to the E-surface, were employed. The premature optimum indicated for this run was caused, presumably, by the same basic reason as in Runs 4 and 5: The penalty for being too close to critical restraints was so light that the optimization could progress very close to these restraint surfaces--so close that, apparently, slight inaccuracies in gradient component calculations, or relatively large steps, or/and critical restraint functions decreasing too rapidly caused violation of some restraint(s). By means of the automatic reduction schedule built into the logic diagram of Figure 15, a premature optimum resulted.

APPENDIX VIII.

APPLICATION OF THE CRST IN OPTIMIZATION PROBLEMS

This appendix consists of: rules and observations concerning the use of the CRST, application of the CRST to the general linear programming problem, a modified procedure for using the CRST, use of the CRST in the experimental attainment of optimum conditions in the laboratory and on the industrial scene, and use of the CRST for automatic optimum control in complex systems.

USE OF THE CRST IN OPTIMIZATION PROBLEMS

The following observations and guide rules are suggested in light of limited experience in using the CRST.

1. Based on the outcome of Runs 4, 5, and 6, it is probably desirable to let the solution progress as nearly as possible up through the very middle of the solution space. This can be done by careful choice of initial feasible conditions, appropriate selection of the $\underline{W}_i$'s, and a suitable schedule of reduction for $\underline{r}$. The penalty should, during the early stages of the optimization, be sufficient to compel solutions to be well within the restraining boundaries and somewhat below the E-surface. However, the last few values of $\underline{r}$ before $\underline{r} = 0$ must be such that the effectiveness surface is closely approached. Then the final ascent on the E-surface is short and leads, presumably, to a more optimal solution.

   If the optimization commences on an A-surface which

is (because of initially small values of $\underline{r}$ or $\underline{W_i}$'s) pressed too closely to the restraint, misleading gradients, taken on slight rolls in the created response surface or involving branches of the $\underline{A}$-functions outside the solution space, can easily result in restraint violations. The smaller steps and the greater number of gradient calculations which would then have to be taken would cause considerable inefficiency in the method. It should be noted that as $\underline{r}$ is reduced, the smoothing effect resulting from the composite nature of the $\underline{A}$-function is likewise reduced, and irregularities in the surface are probably more likely.

2. After an optimum is determined, it is important to check to see whether a significantly better or different optimum, involving a shorter ascent on the $\underline{E}$-surface, could result if the uppermost $\underline{A}$-surface were allowed to approach even more closely to the $\underline{E}$-surface (see discussion of Runs 3, 7, and 8). This can be accomplished by letting the last value of $\underline{r}$, before $\underline{r} = 0$, become even smaller, and then repeating the final portion of the optimization. It should be noted that a good last value of $\underline{r}$ ($\underline{r} > 0$) depends on, among other things, the number of critical or near critical restraints.

3. The functional form of individual restraints should probably be such that the range of values that any $\underline{R_i}$ is likely to assume is relatively small. (See discussion of Runs 4 and 5.)

4. When the components of the gradients must be approximated, it appears advisable to do so as accurately as possible. This may avoid difficulties where optima lie in regions characterized by large changes in slopes. (See discussion of Runs 1 and 2.) Also, more accurately approximated gradient components help to minimize the chance of calculations involving branches of the A-functions outside the solution space.

5. Certain changes in the detailed logic diagram (see Figure 15) would seem to facilitate automatic computation. One such change could allow for very large steps to be taken initially during any ascent so that as much progress as possible could be quickly made. When these large steps overstep the restraint boundaries or the maxima, their size could be reduced by an appropriate schedule.

   Another change would be to consider, along with the size of h, the effect of the magnitude of the components of the gradient in determining step size.

   Still another change would be to circuit gradient component approximations through the feasibility check so as to avoid misleading calculations involving invalid branches of the A-functions.

6. For very large programs, it may be necessary to sacrifice some of the automatic features of Figure 15. Such a program would than calculate as a minimum, E and the restraints, and leave the gradient calculations, etc., to

the operator who would then feed in new input at each step of the optimization.

7. It is possible that for some types of problems, the functional form of the penalty portion of the A-functions could profitably be changed.

8. Finally, of course, the complications of interpretation during optimization associated with the Method of Steepest Ascents (10, 13) apply also to the CRST.

Again, since the A-functions are a composite of the effectiveness and restraint functions, they are probably smoother in general than these functions (except when r is very small). This smoothing effect might lessen the interpretive difficulties sometimes accompanying the use of the Method of Steepest Ascents. Any smoothing, however, is gained at the expense of developing a more complex A-function, especially if there are a number of complicated functional restraints. One way to simplify this situation is to try, as a result of preliminary, partial optimizations, to eliminate what appear to be noncritical restraints.

9. As in the Method of Steepest Ascents, it is worthwhile as a check, to try to attain a given optimum from a different starting point or by a different path, or, possibly, by using a different solution technique. In addition, one can "cast about" randomly at a given optimum to explore the possibility of alternate optima [see, e.g., (13)].

APPLICATION TO LINEAR PROGRAMMING

It is interesting to consider the application of the CRST to the general linear programming problem:*

Maximize:
$$\underline{E} = \sum_{\underline{j}=1}^{\underline{n}} \underline{c_j x_j}^{**}$$

subject to
$$\sum_{\underline{j}=1}^{\underline{n}} \underline{a_{ij}}\ \underline{x_j} \geq \underline{b_i}, \quad \underline{i} = 1,2,\ldots\ldots, \underline{m}$$

or
$$\underline{R_i} = \left(\sum_{\underline{j}=1}^{\underline{n}} \underline{a_{ij}}\ \underline{x_j} \right) - \underline{b_i} \geq 0, \quad \underline{i} = 1,2,\ldots\ldots, \underline{m}$$

and
$$\underline{R'_j} = \underline{x_j} \geq 0, \quad \underline{j} = 1,2,\ldots\ldots, \underline{n}.$$

Then
$$\underline{A} = \underline{E} - \underline{r} \left[\sum_{\underline{i}=1}^{\underline{m}} \frac{\underline{W_i}}{\underline{R_i}} + \sum_{\underline{j}=1}^{\underline{n}} \frac{\underline{W'_j}}{\underline{R'_j}} \right]$$

$$= \sum_{\underline{j}=1}^{\underline{n}} \underline{c_j}\ \underline{x_j} - \underline{r} \left[\sum_{\underline{i}=1}^{\underline{m}} \frac{\underline{W_i}}{\left(\sum_{\underline{j}=1}^{\underline{n}} \underline{a_{ij}}\ \underline{x_j} \right) - \underline{b_i}} + \sum_{\underline{j}=1}^{\underline{n}} \frac{\underline{W'_j}}{\underline{x_j}} \right],$$

---

* For an introduction to linear programming, see (1).

**Here the $\underline{x_j}$'s include no artificial or slack variables. The $\underline{c_j}$'s, $\underline{a_{ij}}$'s, and $\underline{b_i}$'s are constants.

and the gradient components become

$$\frac{\partial A}{\partial x_j} = c_j + r \sum_{i=1}^{m} \frac{W_i a_{ij}}{(R_i)^2} + \frac{W'_j}{(R''_j)^2} \quad , j = 1,2,\ldots, n.$$

Perhaps by creating and storing current $W_i/(R_i)^2$ and $W''_j/(R'_j)^2$ values, by working rowwise and columnwise in separate computational operations, and by taking advantage of the implications of linearity, the CRST might allow for an efficient (though approximate) solution to some linear programming problems.

AN ALTERNATE METHOD OF OPTIMIZING BY THE CRST

It is possible that the CRST can be employed in a slightly different manner to obtain optimum solutions. Using the CRST as described in previous sections, the optimum value of E is actually the limiting value of the maxima of the A-functions (assumed to have continuous first partial derivatives) as r approaches 0. Any A-function can be written:

$$A = A(x_1, x_2, \ldots, x_n; r).$$

The n independent variables (x_i's) corresponding to the maximum of a given A-surface (characterized by a given value of r) are expressed implicitly as the appropriate solution of the n equations:

$$\partial A/\partial x_i = 0; \quad i = 1,2,\ldots, n.$$

Theoretically, one could explicitly solve for the values of each of the x_i's in any set of x_i giving the maximum value of A for any

A-surface (i.e., for any value of r). Let such a set of maximal x_i be:

$$(x_i)_{m,r} = f_i(r), \quad i = 1,2,\ldots, n.$$

Let the set of optimal values of $(x_i)_{m,r}$ be:

$$(x_i)_{m,r=o}, \quad i = 1,2,\ldots. n.$$

This set of optimal values is the solution to the optimization problem. The optimal value of each variable can be found as follows:

$$(x_i)_{m,r=o} = \lim_{r \to o} (x_i)_{m,r} = \lim_{r \to o} f_i(r).$$

To explicitly develop each $f_i(r)$ as above would be impractical if not impossible. However, there is an experimental counterpart to the above process. This consists in applying the original version of the CRST to determine, very accurately, several sets of maximal x_i's corresponding to several A-surface maxima, each characterized by a given value of r. Then, graphically or analytically, each variable can independently be expressed as a function of r alone. The resulting functions are approximations of the $f_i(r)$. Let these approximate functions be designated by $f'_i(r)$. The optimal values of the independent variables can thus be approximated by:

$$(x_i)_{m,r=o} \cong \lim_{r \to o} f'_i(r).$$

The resulting approximate optimal solution can then be fed as input to a computer. If the solution is feasible, further progress could be made in the conventional manner on the E-surface. If the approximate optimal solution is not feasible, the values of the independent variables could be changed by selecting "optimal" solutions corresponding to small, positive values of r. The value of r would be increased only enough to just allow a feasible solution. Then, as above, the conventional

procedure could be used to find an improved, approximate optimum.

It should be noted that this modification of the CRST, like the original version, depends on the possibility of accurately approximating A-surface maxima.

EXPERIMENTAL ATTAINMENT OF OPTIMUM CONDITIONS FOR NONLINEAR, RESTRAINED SYSTEMS

In addition to its application to the optimization of fully developed models, the CRST can be applied in situations where a portion or all of a nonlinear, restrained system is unquantified. This can be done in a sequential analysis by the experimental determination of the necessary effectiveness and restraint response (rather than the calculation of these from a model) followed by the estimation of the gradient components required. [It should be recalled that the CRST can be thought of as converting a restrained optimization problem into a series of nonlinear, unrestrained problems, each of which can be solved by the Method of Steepest Ascents. The use of the Method of Steepest Ascents in experimental designs has been studied to a considerable extent (10).]

The extrapolation modification of the CRST described in the previous section could be of particular value in the experimental optimization of nonlinear, restrained systems.

"EVOLUTIONARY OPERATION" AND THE CRST

Essentially, Evolutionary Operation is the application of experimental optimization techniques to full-scale industrial operations so as to allow gradual adjustment to optimum operating conditions without disrupting production significantly (53, 54). The Method of Steepest

Ascents is used in present applications of Evolutionary Operation to complicated nonlinear, but unrestrained, systems. The CRST could be used in applications to general nonlinear, restrained systems.

CONTINUOUS OPTIMIZATION OF NONLINEAR, RESTRAINED SYSTEMS BY AUTOMATIC CONTROLLERS

As uncontrolled variables or parameters of a system change, values of the independent, controllable variables giving optimum operation also change. Automatic optimization controllers [see, e.g., (55)] continuously monitor a system and apply experimental means of optimization in a continuous and automatic Evolutionary Operation (see above). In this way, near-optimum conditions are always maintained. The Created Response Surface functions could allow the use of such automatic optimization controllers to be extended to nonlinear, restrained systems.